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PB-273 196

Analysis of a Series of Samples for Polybrominated Bephenyls (PBBs)

Research Triangle Inst, Research Triangle Park, N C

Prepared for

Environmental Protection Agency, Washington, D C Office of Toxic Substances

Aug 77

EPA-560/6-77-020

PB 273 196

ANALYSIS OF A SERIES OF SAMPLES FOR POLYBROMINATED BIPHENYLS (PBBs)

AUGUST 1977

ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF TOXIC SUBSTANCES
WASHINGTON, D.C. 20460

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TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA-560/6-77-020	2.	3. RECIPIENT'S ACCESSION NO. PB273196
4. TITLE AND SUBTITLE Analysis of a Series of Samples for Polybrominated Biphenyls (PBBs)		5. REPORT DATE Prepared August, 1977 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) M. D. Erickson, R. A. Zweidinger and E. D. Pellizzari		8. PERFORMING ORGANIZATION REPORT NO. Task V Final Report
9. PERFORMING ORGANIZATION NAME AND ADDRESS Research Triangle Institute Post Office Box 12194 Research Triangle Park, North Carolina 27709		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. EPA 68-01-1978
12. SPONSORING AGENCY NAME AND ADDRESS Office of Toxic Substances U. S. Environmental Protection Agency Washington, D. C. 20460		13. TYPE OF REPORT AND PERIOD COVERED Final March 10 - June 18, 1977 14. SPONSORING AGENCY CODE 500/00
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

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Three commercial samples of decabromobiphenyl ether ($C_{12}Br_{10}O$) were analyzed for impurities by GC/MS using the same conditions as for the higher PBBs. All three samples contained $C_{12}Br_9ClO$ in small amounts and one sample contained traces of $C_{12}H_2Br_8O$ and $C_{12}HBr_9O$.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Polybrominated Biphenyls PBBs GC/MS Decabromobiphenyl ether Brominated organics		
18. DISTRIBUTION STATEMENT Release unlimited	19. SECURITY CLASS (This Report) unclassified	21. NO. OF PAGES 69
	20. SECURITY CLASS (This page) unclassified	22. PRICE PC A04 / MF A01

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

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Methods for the analysis of polybrominated biphenyls (PBBs) by gas chromatography/mass spectrometry/computer (GC/MS/COMP) were developed using a 45 cm x 0.2 cm i.d. glass column packed with 2% OV-101 coated on Gas-Chrom Q. The column was programmed from 150-300°C at 20°C/min for the chromatography of mono- through pentabromobiphenyl and from 220-300°C at 12°C/min for hexa- through decabromobiphenyl. Two separate analyses were required to adequately separate the lower isomers and to yield definitive peaks for the higher isomers. A total of 80 samples were analyzed by GC/MS in the Multiple Ion Detection (MID) mode. They contained from undetectable to 860 µg/ml of PBBs. The higher isomers accounted for the majority of the PBBs found. Mass spectra obtained during GC/MS analysis of some of the more highly concentrated samples not only confirmed the presence of PBBs, but also detected polybrominated biphenyl ethers and other brominated compounds.

Three commercial samples of decabromobiphenyl ether ($C_{12}Br_{10}O$) were analyzed for impurities by GC/MS using the same conditions as for the higher PBBs. All three samples contained $C_{12}Br_9ClO$ in small amounts and one sample contained traces of $C_{12}H_2Br_8O$ and $C_{12}HBr_9O$.

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ACKNOWLEDGEMENTS

The authors wish to thank Drs. J. T. Bursey, D. Rosenthal and M. E. Wall and Mr. L. Kelner of the Research Triangle Institute (RTI) for their assistance and encouragement and Drs. V. J. DeCarlo and G. E. Parris, Environmental Protection Agency, Office of Toxic Substances, Washington, D. C. for their valuable discussions. We also wish to thank Messrs. C. L. Stratton and S. A. Whitlock of Environmental Sciences and Engineering (ES&E), Incorporated, Gainesville, Florida whose earnest participation in the sample collection and preparation was vital to the successful completion of this cooperative effort.

LIST OF ABBREVIATIONS

ES&E	-	Environmental Sciences and Engineering, Inc., Gainesville, Florida
GC	-	Gas Chromatography
GC/MS	-	Gas Chromatography/Mass Spectrometry/Computer
M	-	Parent Ion in Mass Spectrum
m/e	-	Mass-to-charge ratio
MID	-	Multiple Ion Detection
OCN	-	Octachloronaphthalene
PBB	-	Polybrominated biphenyls
RMR	-	Relative Molar Response
RSD	-	Relative Standard Deviation
SD	-	Standard Deviation
TIC	-	Total Ion Current

1.0 INTRODUCTION

Polybrominated biphenyls (PBBs) are used extensively as flame retardants for polymers, textiles, and other materials.[1] The major component of the most common commercial mixture, Fire Master PB-6®[2], is hexabromobiphenyl.[3-7] Concern about the environmental impact and health effects of wide spread use of PBBs has been aroused by a recent major environmental catastrophe in Michigan.[4-8] Their chemical similarity to polychlorinated biphenyls (PCB) and polychlorinated naphthalenes (PCN) has raised the question of bioconcentration and toxicity to the point to warrant a test of the carcinogenicity of hexabromobiphenyl by the National Cancer Institute Bioassay Program.[9]

Spurred by the Michigan disaster, analytical methodologies have been developed and applied to feeds[5], dairy products[4] and soils.[6,7] Although extensive analytical work is being carried out with respect to samples originating in Michigan, little attention has been directed at more generalized pollution resulting from normal manufacture and use of PBBs throughout the United States. This research was designed to study potential industrial sources of PBBs and to assess their environmental occurrence.

2.0 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

Methods for the analysis of polybrominated biphenyls (PBBs) by gas chromatography/mass spectrometry/computer (GC/MS/COMP) were developed. Mono- through pentabromobiphenyls were analyzed using a 45 cm x 0.2 cm i.d. glass column packed with 2% OV-101 coated on Gas-Chrom Q and a flow rate of 30 cc/min helium. The column temperature was 150° initially, raised at 25°/min to 300°, then held constant. Hexa- through decabromobiphenyls were analyzed using the same gas chromatographic (GC) conditions as for the lower isomers except the flow rate was 20 cc/min and the column temperature was 220° initially, programmed at 12°/min to 300°, then held constant. Samples were analyzed using the mass spectrometer in the Multiple Ion Detection (MID) mode to achieve greater sensitivity.

A total of 87 samples were received from Environmental Sciences and Engineering (ES&E), Gainesville, Florida who collected, extracted, and added an external standard to the samples (EPA Contract No. 69-01-3248). The samples received included not only extracts of environmental samples, but also blanks, spikes, duplicates, etc. for quality control purposes.

The samples were analyzed for PBBs (both high and low levels of bromination). The total amounts of PBBs found ranged from undetectable to 860 µg/ml. The higher isomers accounted for the majority of the PBBs found.

Mass spectra obtained during GC/MS analysis of some of the more highly concentrated samples confirmed the presence of PBBs and polybrominated biphenyl ethers and other brominated aromatics were also identified.

Three commercial samples of decabromobiphenyl ether ($C_{12}Br_{10}O$) were analyzed by GC/MS to determine if impurities were present. The gas chromatographic conditions were the same as those used for the higher PBBs. All three samples were found to contain $C_{12}Br_9ClO$ in small amounts and one sample contained traces of $C_{12}H_2Br_8O$ and $C_{12}HBr_9O$. Further research in

this area should be directed at the unusual fragmentation of decabromobiphenyl ether observed in the mass spectra. The trace impurities present in decabromobiphenyl ether could best be further investigated by high performance liquid chromatographic fractionation of large amounts of the sample to concentrate these impurities for mass spectrometric identification.

3.0 OBJECTIVES

The major emphasis of this research was to analyze a series of environmental samples for PBBs by GC/MS. The specific objectives were to (1) develop gas chromatographic conditions which separated the PBB components and elutes the compounds of interest within a short time with definitive, easily quantifiable peaks; (2) develop a quantification procedure for the PBBs found in the samples; (3) analyze the samples; (4) interpret the data; (5) confirm the presence of PBBs in some of the more highly concentrated samples; and (6) analyze three samples of commercially available decabromobiphenyl ether to determine gas chromatographable impurities.

4.0 METHOD DEVELOPMENT

Methods were developed for the analysis of PBBs by GC/MS using a short GC column. Each sample was analyzed twice, once separating the lower isomers and once eluting the higher isomers quickly to provide sharp peaks for detection and quantitation. Preliminary investigation using direct probe mass spectrometry for analysis of samples was shown not to be feasible. The development of analytical conditions is discussed in detail below.

4.1 EXPERIMENTAL APPARATUS, INSTRUMENTS AND CHEMICALS

Toluene (Burdick and Jackson, Muskegon, Michigan) was redistilled prior to use. Polybrominated biphenyls (4-bromobiphenyl, 4,4'-dibromobiphenyl, 2,2',5-tribromobiphenyl, 2,2',5,5'-tetrabromobiphenyl, 2,2',4,5,6-pentabromobiphenyl, 2,2',4,4',5,5'-hexabromobiphenyl, 2,2',3,3',5,5',6,6'-octabromobiphenyl, and decabromobiphenyl) and octachloronaphthalene were purchased from RFR Corporation, Hope, Rhode Island.

Analysis of all samples was accomplished using a Finnigan 3300 quadrupole GC/MS equipped with a PDP/12 computer. Direct probe analysis of a decabromobiphenyl ether sample was accomplished using an AEI MS 902 high resolution mass spectrometer. Complete descriptions of the instruments are presented in Appendix A.

4.2 DIRECT PROBE MASS SPECTROMETRIC ANALYSIS OF PBBs

Initial experiments using direct probe mass spectrometry indicated that this technique potentially could be an easy, sensitive, and very quick method of analyzing samples for the higher order PBB isomers. This avenue was pursued because these isomers were found to chromatograph poorly when using instrumental conditions for the analysis of PCBs and PCNs. Although the sensitivity of the direct probe for standards was excellent (<0.5 ng) and the sample analysis was completed within about 2-3 minutes (Figure 1), the procedure was non-reproducible. Furthermore, it suffered from non-specificity for environmental samples.

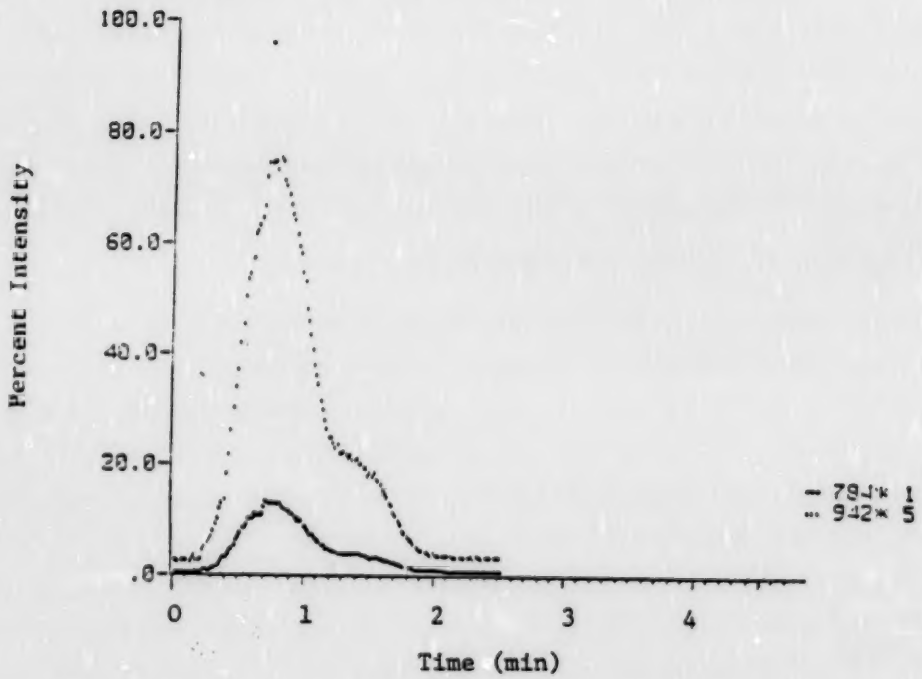

Figure 1. Plot of ion intensities vs. time during direct probe mass spectrometry analysis of "Soil Extract/Hexane Spiked" sample.

4.3 GC/MS/COMP ANALYSIS OF HIGHLY BROMINATED PBBs

Initial experiments indicated that, under the conditions necessary for resolution of the lower brominated PBBs, the highly brominated PBBs had long retention times and eluted as broad, diffuse peaks. Since such broad peaks were not conducive to quantification and reduced the sensitivity of the analysis, GC conditions were sought which eluted these compounds quickly as definitive peaks. These conditions, which were adopted for the analysis of samples, required a 45 cm x 0.2 cm i.d. glass column packed with 2% OV-101 coated on Gas-Chrom Q and a flow rate of 20 cc/min helium. The temperature of the molecular separator was 280°, the injection port 270°, and the GC column 220° initially, and then programmed at 12°/min to 300°. Under these conditions, hexa-, hepta-, octa-, nona-, and decabromobiphenyls and the octachloronaphthalene standard were resolved as definitive peaks. Decabromobiphenyl eluted within 6 min (Figure 2, Table 1). Hepta- and nonabromobiphenyl were not commercially available, but were found to be impurities in the standards. As seen in Figure 2, both isomers of nona-bromobiphenyl are present, with retention times of 4.6 and 5.2 min.

The mass spectrometer ionization volatage was 70 eV (nominal) and the electron multiplier voltage was between 1.8-2.2 kV. The spectrometer was either scanned from m/e 100-1000 or used in the MID mode as discussed below.

4.4 GC/MS/COMP ANALYSIS OF LOWER BROMINATED PBBs

Gas chromatographic conditions were developed for separating the lower (mono- through penta-) brominated PBBs which also eluted the higher isomers within a reasonable time in preparation for another injection. The GC/MS conditions were the same as described above, except the column temperature was 150° initially, raised at 20°/min to 300°, then held constant, and the flow rate was 30 cc/min. Figure 3 and Table 2 illustrate the separations and retention times obtained under these conditions.

4.5 SELECTION OF m/e IONS FOR MID ANALYSIS

Multiple ion detection (MID) is an operational mode for gas chromatograph/mass spectrometers where several m/e values are monitored through the chromatogram. To obtain each m/e value preset voltages are step-jumped at short time intervals. Since this technique also allows integration of ion

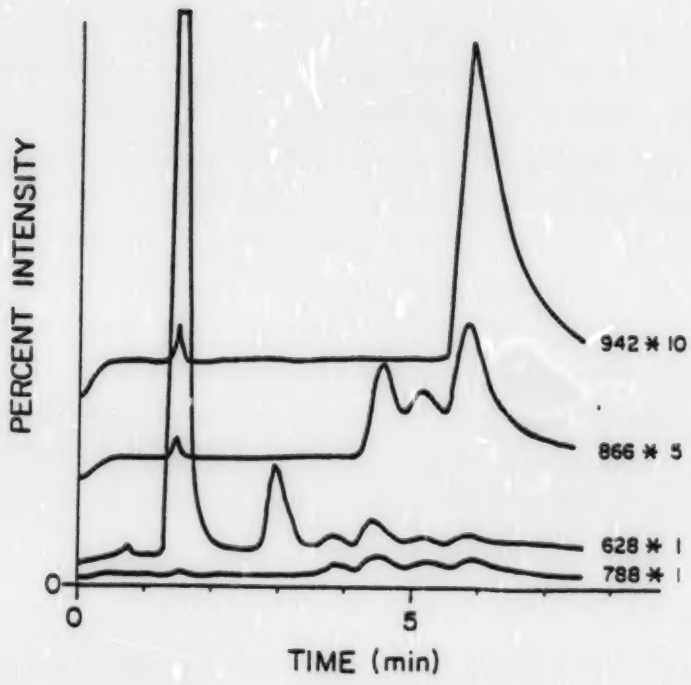

Figure 2. MID chromatograms from GC/MS analysis of hexa-, octa-, and decabromobiphenyl standard. Note: nonabromobiphenyl impurities (m/e 866).

Table 1. RETENTION TIMES FOR PBB STANDARDS USING GC CONDITIONS FOR HIGHER ISOMERS[a]

Compound	Retention Time (min)[b]
octachloronaphthalene (standard)	1.3
2,2',4,4',5,5'-hexabromobiphenyl	1.7
heptabromobiphenyl[c]	3.1
2,2',3,3',5,5',6,6'-octabromobiphenyl	3.8
nonabromobiphenyl[c]	4.4
decabromobiphenyl	5.8

[a]See Figure 2 for MID chromatogram. See text for conditions.

[b]In cases where more than one isomer was present due to impure standards, the retention time was listed for most intense peak.

[c]Impurities in standards; positional isomers not identified.

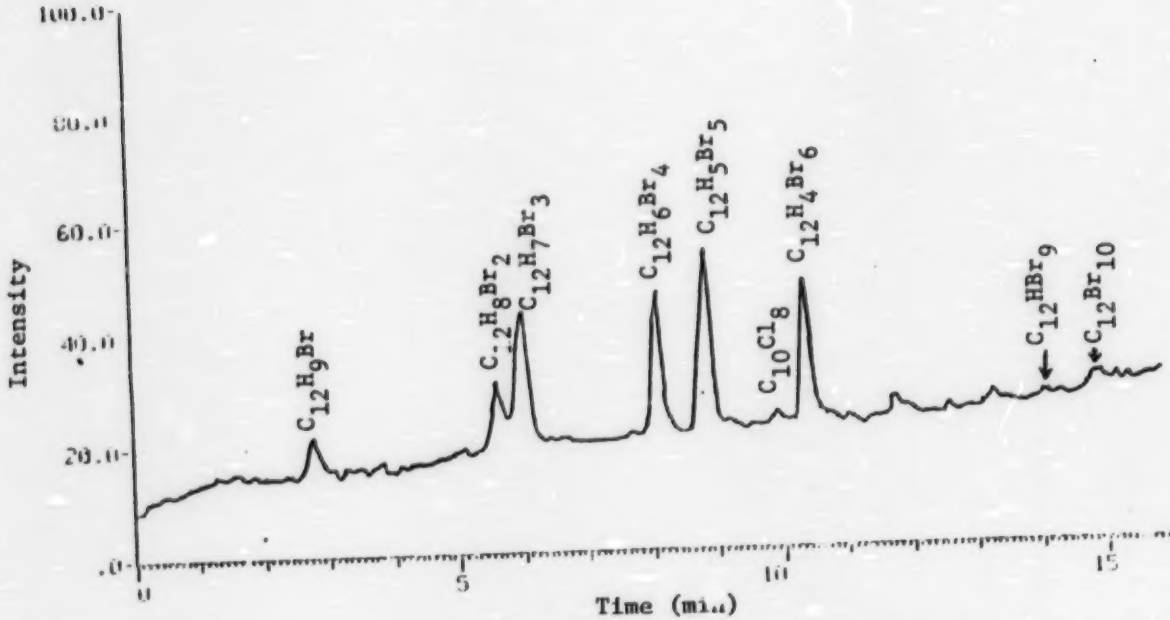

Figure 3. Total ion current chromatogram of mixed PBB standard ca. 150 rg of each compound.

Table 2. RETENTION TIMES FOR STANDARDS[a] USING GC CONDITIONS FOR LOWER ISOMERS

Compound	Retention Time (min)
4-bromobiphenyl	2.7
4,4'-dibromobiphenyl	5.6
2,2',5-tribromobiphenyl	5.9
2,2',5,5'-tetrabromobiphenyl	8.0
2,2',4,5,6-pentabromobiphenyl	8.8
octachloronaphthalene	9.9
2,2',4,4',5,5'-hexabromobiphenyl	10.3
heptabromobiphenyl[b]	11.7
2,2',3,3',5,5',6,6'-octabromobiphenyl	13.2
nonabromobiphenyl[b]	14.1
decabromobiphenyl	14.7

[a]See Figure 3 for TIC chromatogram. Conditions for lower isomers, see text.

[b]Impurities in standards; positional isomers not identified.

intensity for a longer time period for the desired ions than in the customary full-scan mode, the sensitivity of the instrument generally is increased by approximately two orders of magnitude. By judicious selection of m/e values for monitoring specific compounds, interference by unwanted compounds can usually be minimized.

Eight m/e ions were selected for monitoring the PBBs with the ninth channel devoted to detection of the octachloronaphthalene external standard (Table 4). Ions were chosen from the parent cluster even though they were not necessarily the most intense to reduce the probability of interference from fragments of other PBBs or compounds.

The m/e ions selected were generally those most intense in the parent cluster. The natural abundance of two major bromine isotopes (atomic weights of 79 and 81) yields a cluster of ions with the different isotopic permutations as shown in Table 3. This table illustrates clearly that the parent ion (M) was not nearly as intense as ions at or near the centroid of the cluster.

The m/e ions selected for MID analysis are shown in Table 4. Two m/e ions are listed for each isomer and to the extent possible, both ions were used to confirm the presence of brominated compounds. The relative intensity of the two m/e ions as calculated from the theoretical isotopic abundance was used for comparing and confirming the identity and purity of the PBBs monitored in environmental samples.

4.6 SELECTION OF EXTERNAL STANDARD

Octachloronaphthalene (OCN) was selected as an external standard based on its similar retention time to the middle isomers of the PBBs, its high molecular weight, unique parent ion, and low likelihood of occurrence in these environmental samples. The environmental occurrence of OCN has been shown to be relatively infrequent even in areas where high concentrations of other polychlorinated naphthalenes were observed.[11] The high molecular weight and unique parent ion of OCN reduced the chance of interference from background or sample components. In addition, the low volatility of OCN decreased the possibility of loss prior to analysis.

Table 3. INTENSITIES OF ISOTOPIC PEAKS RELATIVE TO THE MOLECULAR ION FOR POLYBROMINATED COMPOUNDS

Degree of Bromination	M	M + 2	M + 4	M + 6	M + 8	M + 10	M + 12	M + 14	M + 16	M + 18	M + 20
Br	100	97.8									
Br_2	100	195	95								
Br_3	100	293	286	93							
Br_4	100	391	575	375	92						
Br_5	100	489	958	937	459	90					
Br_6	100	587	1436	1875	1376	539	88				
Br_7	100	685	2011	3280	3210	1885	615	86			
Br_8	100	783	2682	5249	6421	5027	2460	687	84		
Br_9	100	881	3440	7873	11557	11310	7379	3095	757	82	
Br_{10}	100	979	4310	11247	19262	22620	18447	10315	3786	823	81

Table 4. MID IONS SELECTED FOR PBB ANALYSIS

PCB Isomers	M[a]	MID Ions[b]
$C_{12}H_9Br$	232	232, 234
$C_{12}H_8Br_2$	310	312, 310
$C_{12}H_7Br_3$	388	390, 392
$C_{12}H_6Br_4$	466	470, 472
$C_{12}H_5Br_5$	544	548, 550
$C_{12}H_4Br_6$	622	628, 630
$C_{12}H_3Br_7$	700	706, 708
$C_{12}H_2Br_8$	778	788, 784
$C_{12}HBr_9$	856	866, 862
$C_{12}Br_{10}$	934	942, 946

[a] M = nominal molecular weight based on Br = 79

[b] Ions listed in order of "primary" and "secondary"

4.7 QUANTITATION

Quantitation was achieved by comparing the computer-calculated integrated area of the PBB isomers with the integrated response for a known amount of octachloronaphthalene. To compensate for differences in ionization cross-section, the relative molar response of available PBB standards was obtained.

The calculation of the relative molar response (RMR) factor allows the estimation of the levels of sample components without establishing a calibration curve. The RMR is calculated as the integrated peak area of a known amount of the compound, A°_{unk}, with respect to the integrated peak area of a known amount of standard, A°_{std} (in this case octachloronaphthalene), according to the equation

$$RMR = \frac{A^{\circ}_{unk}/moles_{unk}}{A^{\circ}_{std}/moles_{std}} = \frac{(A^{\circ}_{unk})(mw_{unk})(g_{std})}{(A^{\circ}_{std})(mw_{std})(g_{unk})} \quad \text{(Equation 1)}$$

From this calculated value, the concentration of an identified compound in a sample is calculated by rearranging Equation 1 to give

$$g_{unk} = \frac{(A_{unk})(mw_{unk})(g_{std})}{(A_{std})(mw_{std})(RMR)} \quad \text{(Equation 2)}$$

The use of RMR for quantitation by GC/MS has been successful in repeated applications to similar research problems.[10-12]

The RMRs for the available PBB isomers were calculated from the numerical integrations of peaks observed in the appropriate MID channel. The RMRs listed in Table 5 are mean values of three injections of each of three replicate standard mixtures. The standard of 2,2',3,3',5,5',6,6'- octabromobiphenyl was found to be severely contaminated by hepta- and nonabromobiphenyl isomers, so they were not used in the RMR calculations. The RMR values listed for hepta-, octa-, and nonabromobiphenyl were calculated from a linear interpolation between the RMR values obtained for hexa- and decabromobiphenyl.

Several qualifications must be recognized regarding the RMR values presented in Table 5. The values obtained for these positional isomers were probably not highly precise for other isomers since differences in the

Table 5. RELATIVE MOLAR RESPONSE VALUES DETERMINED FOR PBBs

Compound	RMR[a]	SD[b]	RSD[c]
4-bromobiphenyl	1.34	0.64	0.48
4,4'-dibromobiphenyl	2.09	0.67	0.32
2,2',5-tribromobiphenyl	1.04	0.35	0.33
2,2',5,5'-tetrabromobiphenyl	1.11	0.30	0.27
2,2',4,5,6-pentabromobiphenyl	1.14	0.30	0.27
2,2',4,4',5,5'-hexabromobiphenyl	1.00	0.33	0.33
heptabromobiphenyl[d]	0.77		
octabromobiphenyl[d]	0.53		
nonabromobiphenyl[d]	0.29		
decabromobiphenyl	0.065	0.023	0.35

[a]Mean Relative Molar Response. Nine determinations: three injections each of three replicate standards.

[b]Standard Deviation

[c]Relative Standard Deviation = SD/RMR

[d]Value obtained by linear interpolation between values for 2,2',4,4',5,5'-hexabromobiphenyl and decabromobiphenyl

ionization cross-section may occur. The purity of the standards in some cases were questionable; a small quantity of nona- and hepta- were found in the decabromobiphenyl and hexabromobiphenyl samples, respectively. Both impurities were judged to be <5% and were ignored for the RMR determinations. The relative molar response depends not only on the ionization cross-section, but also on instrumental parameters, including the ion slit widths, exact mass setting, and electronic drift. These considerations were more pronounced over the wider mass ranges used in PBB analysis. Thus, the accuracy of PBB analysis is highly dependent upon the precise determinations of the RMR factor.

4.8 REPRODUCIBILITY

Two samples were analyzed by multiple injections to check the reproducibility of analysis for the various isomers and over the range of PBB levels found. Table 6 summarizes the results for the triplicate analysis of sample number 6077 for the lower isomers. The reproducibility is better than $\pm$10%. Table 7 illustrates the replicate analyses of sample 6058 for the higher isomers. The lack of reproducibility observed for hexa- and heptabromobiphenyl was attributed to the low concentrations, which approached the detection limit. The reproducibility of the analyses for the higher PBB isomers was somewhat impaired by instrumental instabilities at higher m/e values. It is important to note the agreement between the first analysis and the subsequent analyses which were obtained at different time periods (days). This agreement supports the use of RMR values for quantitation.

Table 6. TRIPLICATE ANALYSIS OF SAMPLE NUMBER 6077 ILLUSTRATING REPRODUCIBILITY FOR LOWER ISOMERS

Analysis	Concentration Found (µg/ml)				
	$C_{12}H_9Br$	$C_{12}H_8Br_2$	$C_{12}H_7Br_3$	$C_{12}H_6Br_4$	$C_{12}H_5Br_5$
First	a	4.92	8.56	--	1.15
Second	a	4.29	8.65	--	1.05
Third	a	3.95	7.84	--	1.00
Mean		4.39	8.34	--	1.05
SD		0.41	0.44		0.097
RSD		0.093	0.053		0.093

[a]Severe hydrocarbon interference prevented its accurate determination. Estimated at about 2 µg/ml.

Table 7. REPLICATE ANALYSIS OF SAMPLE NUMBER 6058 ILLUSTRATING REPRODUCIBILITY FOR HIGHER ISOMERS

Analysis	Concentration Found (µg/ml)				
	$C_{12}H_4Br_6$	$C_{12}H_3Br_7$	$C_{12}H_2Br_8$	$C_{12}HBr_9$	$C_{12}Br_{10}$
First	0.046	0.21	0.76	2.36	85.1
Second	--	--	0.73	2.08	66.6
Third	0.012	0.35	0.97	3.44	104
Fourth	0.023	0.40	0.85	3.86	124
Fifth	0.042	0.17	1.05	3.53	110
Mean	0.030	0.29	0.87	3.06	97.7
SD	0.017	0.11	0.14	0.78	22.3
RSD	0.52	0.39	0.16	0.26	0.23

[a]Second through Fifth analyses performed consecutively. First analysis performed one month earlier.

5.0 SAMPLE RECEIPT

Samples were received from ES&E generally in 1.0 ml conical reaction vials with Teflon®-lined septum caps. Each sample had been spiked with 5 ng/µl octachloronaphthalene as an external standard for retention time correlation and quantification. Samples were shipped in ice and were stored at 5° following receipt. Each sample was logged for quality control purposes (a sample log book was used to record the status of each sample) as it was processed and the receipt and numerical coding confirmed via telephone with personnel at ES&E.

A total of 87 samples were received, as listed in Tables 8 and 9 in Section 6.

6.0 ANALYSIS OF ENVIRONMENTAL SAMPLES FOR PBBs

6.1 SAMPLE ANALYSIS

Using the GC/MS methods discussed in Section 4, the samples were analyzed first for the higher PBB isomers (hexa- through decabromobiphenyl) and then for the lower isomers (mono- through pentabromobiphenyl). On the advice of the Project Officer, some of the samples for which no higher isomers were detected were not analyzed for the lower isomers. In addition, the last batch of samples was received after the period of performance ended and were not analyzed.

The results of the analysis of blanks and spiked samples are presented in Table 8. Table 9 summarizes the results of the analysis of numbered samples and numbered spikes.

A sample of the OCN solution (5 ng/µl) used to spike the samples were obtained for ES&E and compared with the OCN solution (4.9 ng/µl) prepared in house. Replicate analyses of the two samples yielded integrated areas of 485.4 $\pm$ 25.5 and 313.5 $\pm$ 18.2, respectively. Taking into account the calculated concentrations, the OCN sample from ES&E was 1.52 times more concentrated that that prepared in house. Since the value directly affects the concentrations in the sample (see Equation 2), the values in Tables 8 and 9 reflect this correction.

6.2 CONFIRMATION FROM MASS SPECTRAL DATA

Several samples contained sufficient concentrations of PBBs for acquisition of full mass spectra. These analyses confirmed the presence of PBB isomers and several other related compounds were also detected.

Sample number 6077 contained a large number of bromobenzene, bromotoluene, and bromobiphenyl ether species as shown in Table 10. The total ion current (TIC) chromatogram and representative mass spectra are presented in Appendix B.

Table 8. ESTIMATED LEVELS OF PBBs IN BLANK AND SPIKED EXTRACTS

Sample[a]	Amount Found (µg/ml)										
	$C_{12}H_9Br$[b]	$C_{12}H_8Br_2$	$C_{12}H_7Br_3$	$C_{12}H_6Br_4$	$C_{12}H_5Br_5$	$C_{12}H_4Br_6$	$C_{12}H_3Br_7$	$C_{12}H_2Br_8$	$C_{12}HBr_9$	$C_{12}Br_{10}$	Total
Blank Toluene (Nan)	--[c]	--	--	--	--	--	--	--	--	--	--
Toluene Filter Wash	--	--	--	--	--	--	--	--	--	--	--
Toluene Filter Wash	--	--	--	--	--	--	--	--	--	--	--
Toluene Filter Wash	--	--	--	--	--	--	--	--	--	--	--
Toluene Filter Wash	--	--	--	--	--	--	--	--	--	--	--
PUF Extract Spiked	27	>85[d]	54	--	--	0.04	.08	.3	2.1	7.9	>180
PUF Extract Blank	--	--	0.08	--	0.06	0.09	--	--	--	--	0.3
H_2O Extract Spiked	12	51	27	0.09	0.06	0.08	--	--	--	--	90
H_2O Extract Blank	0.05	0.2	0.4	0.09	--	--	--	--	--	--	0.8
Soil Extract Spiked	25[e]	80[e]	44[e]	--	0.09	0.06	0.06	--	2.1	8.8	170
Soil Extract Blank	--	--	--	--	--	--	--	--	--	--	--
Spiking Solution	21[f]	53[f]	26[f]	0.6	0.5	0.6	--	--	--	--	100
Blank Sediment Extract	--	--	--	--	--	--	--	--	--	--	--
Spiked Sediment Extract	13[f]	41[f]	15[f]	5.9	3.5	5.3[f]	--	--	--	--	84
Spiking Solution	--	--	--	--	--	9.1	7.4	1.8	1.2	14	33
Blank-PE-4	NA[g]	NA	NA	NA	NA	--	--	--	--	--	--
Blank-Hex-1	NA	NA	NA	NA	NA	--	--	--	--	--	--
Blank-Hex-2	NA	NA	NA	NA	NA	--	--	--	--	--	--
Blank-Hex-3	NA	NA	NA	NA	NA	--	--	--	--	--	--
Blank Tissue	NA	NA	NA	NA	NA	--	--	--	--	--	--
Blank	NA	NA	NA	NA	NA	--	--	--	--	--	--

Table 8. (Cont'd)

[a]Sample code as received from ES&E. For amounts added see ES&E report for Contract No. 69-01-3248.

[b]In cases where positional isomers were observed, the value presented is a total integration of these isomers.

[c]Undetected

[d]Detector saturated

[e]Average of three determinations

[f]Average of two determinations

[g]NA = not analyzed after consultation with the project officer

Table 9. ESTIMATED LEVELS OF PBBs IN ENVIRONMENTAL SAMPLES

Sample[a]	Amount Found (μg/ml)										
	$C_{12}H_9Br$[b]	$C_{12}H_8Br_2$	$C_{12}H_7Br_3$	$C_{12}H_6Br_4$	$C_{12}H_5Br_5$	$C_{12}H_4Br_6$	$C_{12}H_3Br_7$	$C_{12}H_2Br_8$	$C_{12}HBr_9$	$C_{12}Br_{10}$	Total
6509-SO	0.5	--[c]	--	--	--	T[d]	--	--	--	--	0.6
6701-SO	--	--	--	--	--	T	T	--	--	T	T
6703-SO	--	--	--	--	--	T	--	--	--	--	T
6705-SO	--	--	--	--	--	T	--	--	--	--	T
6709-SO	--	--	--	--	1.6	--	--	--	--	--	1.6
6717-SO	--	--	--	--	--	0.2	0.1	0.6	--	13	14
6718-SO	--	--	--	--	--	0.2	0.7	1.2	2.5	4.0	8.7
6791-SO	--	--	--	--	--	T	--	--	--	--	T
6794-SO	--	--	--	--	--	0.2	--	--	0.4	29	29
6797-SO	--	--	--	--	--	0.9	1.1	1.8	4.9	29	38
6004-SED	--	--	--	--	--	0.5	0.1	--	--	--	0.6
6006-W	NA[e]	NA	NA	NA	NA	--	--	--	--	--	--
6020-SED	--	--	--	--	--	0.1	.1	--	--	--	0.2
6047-W	NA	NA	NA	NA	NA	--	--	--	--	--	--
6054-W	NA	NA	NA	NA	NA	--	--	--	--	--	--
6058-W	--	--	--	--	--	T[f]	0.3[f]	0.9[f]	3.0[f]	98[f]	100[f]
6064-W	--	--	--	--	--	1.4	0.5	0.3	0.3	25	28
6069-W	NA	NA	NA	NA	NA	--	--	--	--	--	--
6077-SED	2[g]	4.4[h]	8.4[h]	--	1.1[h]	7.9	6.8	7.4	4.7	820	860
6079-W	--	--	--	--	0.2	0.6	0.5	0.5	3.0	14	19
6406-SED	NA	NA	NA	NA	NA	--	--	--	--	--	--

Table 9. (Cont'd)

Sample[a]	Amount Found (µg/ml)										
	$C_{12}H_9Br$[b]	$C_{12}H_8Br_2$	$C_{12}H_7Br_3$	$C_{12}H_6Br_4$	$C_{12}H_5Br_5$	$C_{12}H_4Br_6$	$C_{12}H_3Br_7$	$C_{12}H_2Br_8$	$C_{12}HBr_9$	$C_{12}Br_{10}$	Total
6406-Spike SED	NA	NA	NA	NA	NA	4.7	0.3	0.1	0.9	2.7	8.8
6512-W	--	--	--	--	--	--	--	--	--	--	--
6512-W Spike	--	--	--	--	--	T	--	--	--	--	T
6515-W	--	--	--	--	--	0.1	0.1	0.8	0.9	2.6	4.6
6522-SED	NA	NA	NA	NA	NA	--	--	--	--	--	--
6523-SED	--	--	--	--	--	0.6	0.3	--	--	--	0.9
6524-W	--	--	--	--	--	0.1	0.1	0.3	0.3	0.8	1.7
6703-Spike	--	--	--	--	--	4.9	0.5	0.3	0.3	2.7	8.9
6710-A	NA	NA	NA	NA	NA	0.1	--	--	--	--	0.1
6711-A	--	--	--	--	--	0.1	--	--	--	--	0.1
6725-A	--	--	--	--	--	T	--	--	--	--	T
6726-A	--	--	--	--	--	T	--	--	--	--	T
6737-A	--	--	--	--	--	0.1	--	--	--	--	0.1
6738-A	--	--	--	--	--	--	--	--	--	--	--
6766-A	NA	NA	NA	NA	NA	--	--	--	--	--	--
6767-A	NA	NA	NA	NA	NA	--	--	--	--	--	--
6010-TS	--	--	--	--	--	--	--	--	--	--	--
6015-TS	--	--	--	--	--	0.5[i]	0.6[i]	0.8[i]	2.4[i]	13.2[i]	18[i]
6016-TS	--	--	--	--	--	T	--	--	--	--	T
6017-TS	--	--	--	--	--	0.3	--	--	--	--	0.3

Table 9. (Cont'd)

Sample	Amount Found (µg/ml)										
	$C_{12}H_9Br$	$C_{12}H_8Br_2$	$C_{12}H_7Br_3$	$C_{12}H_6Br_4$	$C_{12}H_5Br_5$	$C_{12}H_4Br_6$	$C_{12}H_3Br_7$	$C_{12}H_2Br_8$	$C_{12}HBr_9$	$C_{12}Br_{10}$	Total
6018-TS	NA	NA	NA	NA	NA	--	--	--	--	--	--
6021-TS	--	--	--	--	--	0.1	0.1	0.1	0.9	1.5	2.9
6048-TS	--	--	--	--	--	--	--	0.8	25	470	490
6060-TS	--	--	--	--	--	--	--	--	3.5[1]	41[1]	45[1]
6060-TS-Spike	--	--	--	--	--	3.8[1]	0.5[1]	0.3[1]	3.5[1]	47[1]	55[1]
6080-TS	NA	NA	NA	NA	NA	--	--	--	T	T	T
6081-TS	NA	NA	NNA	NA	NA	--	--	--	--	--	--
6082-TS	--	3	--	--	--	--	--	--	--	--	3
6083-TS	--	--	--	--	--	--	--	--	--	--	--
6084-TS	--	--	--	--	--	0.1	--	--	4.9	62	67
6085-TS	NA	NA	NA	NA	NA	--	--	--	--	--	--
6085-TS-Spike	--	--	--	--	--	7.4	0.6	0.3	0.9	7.6	17
6086-TS	--	--	--	--	--	.06	--	--	--	--	.06
6518-TS	--	--	--	--	--	0.5	--	--	--	--	0.5
6525-TS	NA	NA	NA	NA	NA	--	--	--	--	--	--
6526-TS	NA	NA	NA	NA	NA	--	--	--	--	--	--
6527-TS	NA	NA	NA	NA	NA	0.3	--	--	--	--	0.3
6528-TS	--	--	--	--	--	--	--	--	0.1	1.1	1.3
6519-TS	--	--	--	--	--	T	--	--	0.5	--	0.5

Table 9. (Cont'd)

Sample	Amount Found (µg/ml)										
	$C_{12}H_9Br$	$C_{12}H_8Br_2$	$C_{12}H_7Br_3$	$C_{12}H_6Br_4$	$C_{12}H_5Br_5$	$C_{12}H_4Br_6$	$C_{12}H_3Br_7$	$C_{12}H_2Br_8$	$C_{12}HBr_9$	$C_{12}Br_{10}$	Total
Blank-Clay[j]	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	--
6020-Clay[j]	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	--
6046[j]	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	--
6046-Clay[j]	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	--
6521[j]	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	--
6521-Clay[j]	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	--

[a] Sample Code as received from ES&E - SO = soil, W = water, A = air, TS = tissue, SED = sediment

[b] In cases where positional isomers were observed, the value presented is a total integration of these isomers

[c] Undetectable

[d] Trace (generally <0.1 µg/ml)

[e] NA = not analyzed after consultation with project officer

[f] Mean of five determinations. See Table 7

[g] Value approximate due to severe hydrocarbon interference

[h] Average of three determinations. See Table 6

[i] Interferent with OCN peak. Values are minima

[j] Samples not analyzed. Received from ES&E after end of performance period

Table 10. BROMINATED COMPOUNDS DETECTED IN SAMPLE NUMBER 6077 BY GC/MS ANALYSIS

Compound[a]	Retention Time (min)	
$C_6H_4Br_2$	0.1	
C_2Br_4	0.1	
$C_7H_5Br_3$	2.6	
$C_6H_2Br_4$	3.7	
$C_{12}H_7Br_3$	8.5	
$C_7H_3Br_5$	9.5	
C_6Br_6	10.9	
$C_{12}H_6Br_4$	11.2	
$C_{12}H_6Br_4O$	11.2	
$C_{12}H_5Br_5$	12.1	(0.9-1.8)
$C_{12}H_5Br_5O$	12.1	(1.7)[c]
$C_{12}H_4Br_6$	12.5-12.7	(2.2)
$C_{12}H_4Br_6O$	12.5-12.7	(2.5)
$C_{12}H_3Br_7$	13.3-13.7	(2.8-3.3)
$C_{12}H_3Br_7O$	13.3-13.7	(3.3)
$C_{12}H_2Br_8$	13.8-14.3	(4.0)
$C_{12}H_2Br_8O$	14.1-15.4	(4.7)
$C_{12}HBr_9$	14.3-15.4	(4.7)
$C_{12}HBr_9O$	15.4	
$C_{12}Br_{10}$		(6.0)
$C_{12}Br_{10}O$		(7.5)

[a]The bromobiphenyls were confirmed by comparison of mass spectra and retention times with authentic standards.

[b]GC conditions: 2% OV-101 coated on Gas-Chrom Q; column: 45 cm x 0.2 cm i.d., 20 cc/min helium, 100° initial, programmed at 12°/min to 300°.

[c]Temperature conditions were 220° initial, programmed at 12°/min to 300°, for these values in parentheses.

Analysis by GC/MS of sample number 6058 indicated the presence of the PBBs and polybrominated biphenyl ethers listed in Table 11.

Decabromobiphenyl was confirmed by the mass spectra obtained from GC/MS analysis of sample number 6048.

Table 11. BROMINATED COMPOUNDS IN SAMPLE NUMBER 6058

Compound[a]	Retention Time[b] (min)
$C_{12}H_4Br_6O$	2.3
$C_{12}H_3Br_7O$	3.7
$C_{12}HBr_9O$	4.6-4.9
$C_{12}HBr_9$	4.7-4.9
$C_{12}Br_{10}$	6.2
$C_{12}Br_{10}O$	7.4

[a]The bromobiphenyls were confirmed by comparison of mass spectra and retention times with authentic standards.

[b]GC conditions: 2% OV-101 coated on Gas Chrom Q; column: 45 cm × 0.2 i.d., 20 cc/min helium, 220° initial, programmed at 12°/min to 300°.

7.0 ANALYSIS OF COMMERCIAL DECABROMOBIPHENYL ETHER SAMPLES FOR IMPURITIES

Three commercial samples of decabromobiphenyl ether ("Decabrom", $C_{12}Br_{10}O$) were analyzed by GC/MS and direct probe mass spectrometry for characterization of any potentially toxic impurities.

One sample of decabromobiphenyl ether (DECABROM-PS) was purchased from Polyscience, Inc., Warrington, Pennsylvania, Lot No. 5-46-8.

Another sample was obtained through the courtesy of Great Lakes Chemical Co., West Lafayette, Indiana, "Decabromobiphenyl Oxide, Great Lakes DE-83, Ref. No. NY-8860, 6-2-77". This sample is hereafter referred to as DECABROM-GRL.

The third sample was obtained through the courtesy of Dow Chemical Co., Midland, Michigan, Decabromobiphenyl Oxide, FR 300 BA, Lot No. 06076-2, 2# sample. This sample is hereafter referred to as DECABROM-DW.

Solutions of each sample were prepared at 1 mg/ml in toluene. The samples were subjected to GC/MS/COMP analysis on a Finnigan 3300 system using the chromatographic conditions for the higher PBBs (45 cm x 0.2 cm i.d. glass column packed with 2% OV-101 on Gas-Chrom Q; 220° initial, programmed at 12°/min to 300°; 30 cc/min helium carrier gas).

The samples were found to contain primarily $C_{12}Br_{10}O$ with small amounts of $C_{12}Br_9ClO$. DDECABROM-DW also contained traces of $C_{12}H_2Br_8O$ and $C_{12}HBr_9O$. These results are summarized in Figures C-1 through C-3. Two ion clusters were present in the mass spectrum of $C_{12}Br_{10}O$ and $C_{12}Br_9ClO$ (Figure C-1) which were not readily assignable as fragments of either molecule. These clusters, centered at m/e 692 and m/e 613, do not result from simple debromination or dechlorination of either of the two molecules, so the samples were examined further to determine if additional impurities were present. Close examination of the GC/MS data indicated that these clusters co-eluted

with the other ions attributed to $C_{12}Br_{10}O$ and its fragments. Exact mass measurements (to 4 decimal places) were made by direct probe mass spectral analysis using an AEI MS 902 (see Appenix A for a description of the system). Computerized peak matching found excellent correlation of $C_{11}Br_7$ with the ion cluster centered at m/e 692 and a mixture of $C_{11}Br_6$ and $C_{11}Br_6H$ with the ion cluster centered at m/e 613. Both the GC/MS and direct probe MS data indicated that $C_{11}Br_7$ and $C_{11}Br_6$ are fragments of $C_{12}Br_{10}O$, implying an unusual loss of CO from the diphenyl ether molecule. The origin of the $C_{11}Br_6H$ species remain unidentified.

In summary, the impurities found in three decabromobiphenyl ether samples were $C_{12}Br_9ClO$ (three samples), $C_{12}H_2Br_8O$ (one sample), and $C_{12}HBr_9O$ (one sample).

8.0 REFERENCES

1. G. Sundstrom, O. Hutzinger, S. Safe and V. Zitko, The Science of the Total Environment, 6, 15 (1976).
2. Michigan Chemical Corporation, St. Louis, Michigan.
3. W. H. Gutenmann and D. J. Lisk, J. Agr. Food Chem., 23, 1005 (1976).
4. N. V. Fehringer, J. Ass. Offic. Anal. Chem., 58, 978 (1975).
5. N. V. Fehringer, J. Ass. Offic. Anal. Chem., 58, 1206 (1975).
6. L. W. Jacobs, S.-F. Chou and J. J. Tiedje, J. Agr. Food Chem., 24, 1198 (1976).
7. A. B. Filanow, L. W. Jacobs, and M. M. Mortland, J. Agr. Food Chem., 24, 1201 (1976).
8. L. O. Ruzo, G. Sundstrom, O. Hutzinger and S. Safe, J. Agr. Food Chem., 24, 1082 (1976).
9. Pest. Tox. Chem. News, February 9, 1977, p. 25.
10. E. D. Pellizzari, "Analysis of Organic Air Pollutants By Gas Chromatography and Mass Spectroscopy", Publication No. EPA-600/2-77-100, Contract No. 68-02-2262, 112 pp., June, 1977.
11. M. D. Erickson, R. A. Zweidinger, L. C. Michael and E. D. Pellizzari, Environmental Monitoring Near Industrial Sites: Polychloronaphthalenes, EPA Contract No. 68-01-178, Task 1, Final Report, 1977, submitted.
12. M. D. Erickson, R. A. Zweidinger and E. D. Pellizzari, "Identification and Analysis of Polychlorinated Biphenyls and Other Related Chemicals in Municipal Sewage Sludge Samples", Publication No. 560/6-77-021, Contract No. 68-01-1978, August, 1977.

APPENDIX A

DESCRIPTION OF MASS SPECTROMETERS USED IN THIS PROGRAM

FINNIGAN 3300 GC/MS WITH PDP/12 COMPUTER

The Finnigan 3300 mass spectrometer has a mass range of 1000, with unit resolution over the entire range. Calibration of the system is routinely performed with PC-43 for lower mass ranges and tris(perfluoroheptyl)-a-triazine in the higher ranges.

The PDP/12 computer is on-line with the Finnigan system. Long term storage of data is on LINC tapes or removable disc packs. The computer can subsequently treat stored data in several different ways to facilitate interpretation: (a) a reconstructed gas chromatogram is routinely made to obtain retention times; scan number for a given gas chromatographic peak is obtained by operator interaction with a CRT display; (b) any given mass spectrum or an entire series of scans are corrected for background signal (column bleed, septum bleed, etc.); (c) plots of intensities of specific ions (mass fragmentography) are made from the scan data. This type of information is often useful, when correlated with retention time data, for simplifying the identification of particular compounds. Peak areas are also readily obtainable from these mass chromatograms and can be used to provide quantitative information; (d) normalized mass spectra are plotted, using different types of normalization or amplification factors in order to facilitate identification; (e) hard copy output of normalized data in digital form, with various forms of background correction, is also available.

The GC system in use on the Finnigan mass spectrometer is a Finnigan 9500.

The basic hardware of the PDP/12 consists of an 8K central processor fitted with a teletype, random access disc, CRT display and electrostatic printer/plotter. The interface to the mass spectrometer was custom-designed and built and consists of both analog to digital as well as digital to analog interfaces. The latter involves several unique concepts in interface design, since by using this system it is possible to put the entire mass spectral scanning operation under computer control. Since the data acquisition phase of the spectrometer operation is controlled entirely by the computer, a large number of different types of acquisition protocols have been implemented. For example, in the multiple ion detection mode, up

up to nine individual peaks can be selected within the entire mass spectral range, and acquired for varying time intervals as selected by the operator. In the repetitive scanning mode, scan intervals down to one scan per second are possible with entire scans recorded either on LINC tapes or disc.

All data processing operations are carried out interactively by means of programs stored on the small computer.

AEI MODEL 902 HIGH RESOLUTION MASS SPECTROMETER

The spectrometer is equipped with computerized data acquisition and direct-line access to the Triangle Universities Computation Center (TUCC). The PDP/8 computer on this mass spectrometer is fitted with a teletype, high speed paper tape reader and punch, and random access disc. The mass spectrometer interface is of conventional design, making use of a 15 kHz A/D converter, which is suitable for high resolution data acquisition.

Mass spectra are acquired at high resolution with on-line data reduction to the level of peak intensities and peak times. This information is stored on the disc. Under usual operating conditions, a number of spectra are accumulated on the disc and then are sent en masse to the Triangle Universities Computation Center (TUCC) IBM 370/165 for all further processing. The data are transmitted to TUCC by means of a program specially designed and executed at CLS. The technique employed involves having the PDP/8 simulate an IBM 2780 card reader which is interfaced by a synchronous 2000 Baud modem to the telephone line. The communication protocol employed is standard IBM bi-synchronous communication with the PDP/8 carrying out the entire protocol by suitable software. Once received at TUCC, the data are processed by means of programs developed at CLS, and reports either returned to the laboratory or sent out as required to any of the many terminals located in the TUCC facility.

APPENDIX B

TIC CHROMATOGRAM AND REPRESENTATIVE MASS SPECTRA OF GAS CHROMATOGRAPHIC/MASS SPECTROMETRIC ANALYSIS OF SAMPLE NUMBER 6077

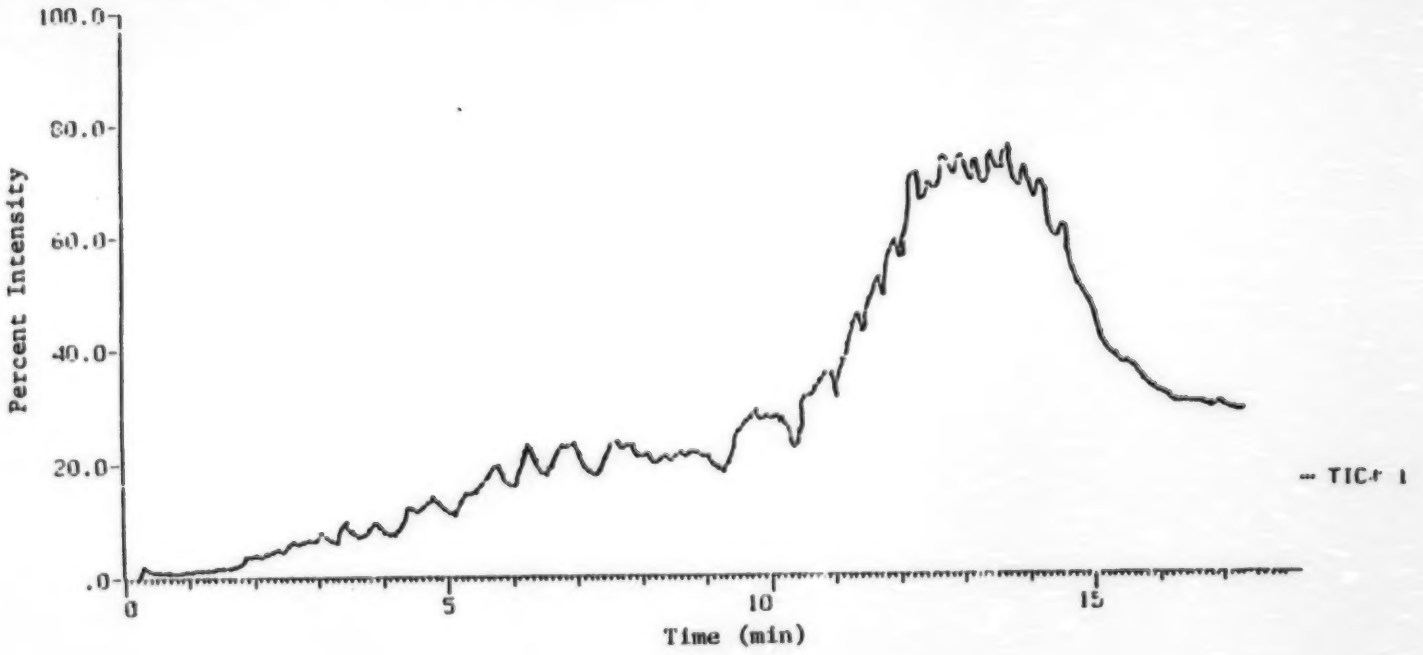

Figure B-1. TIC chromatogram of sample number 6077.

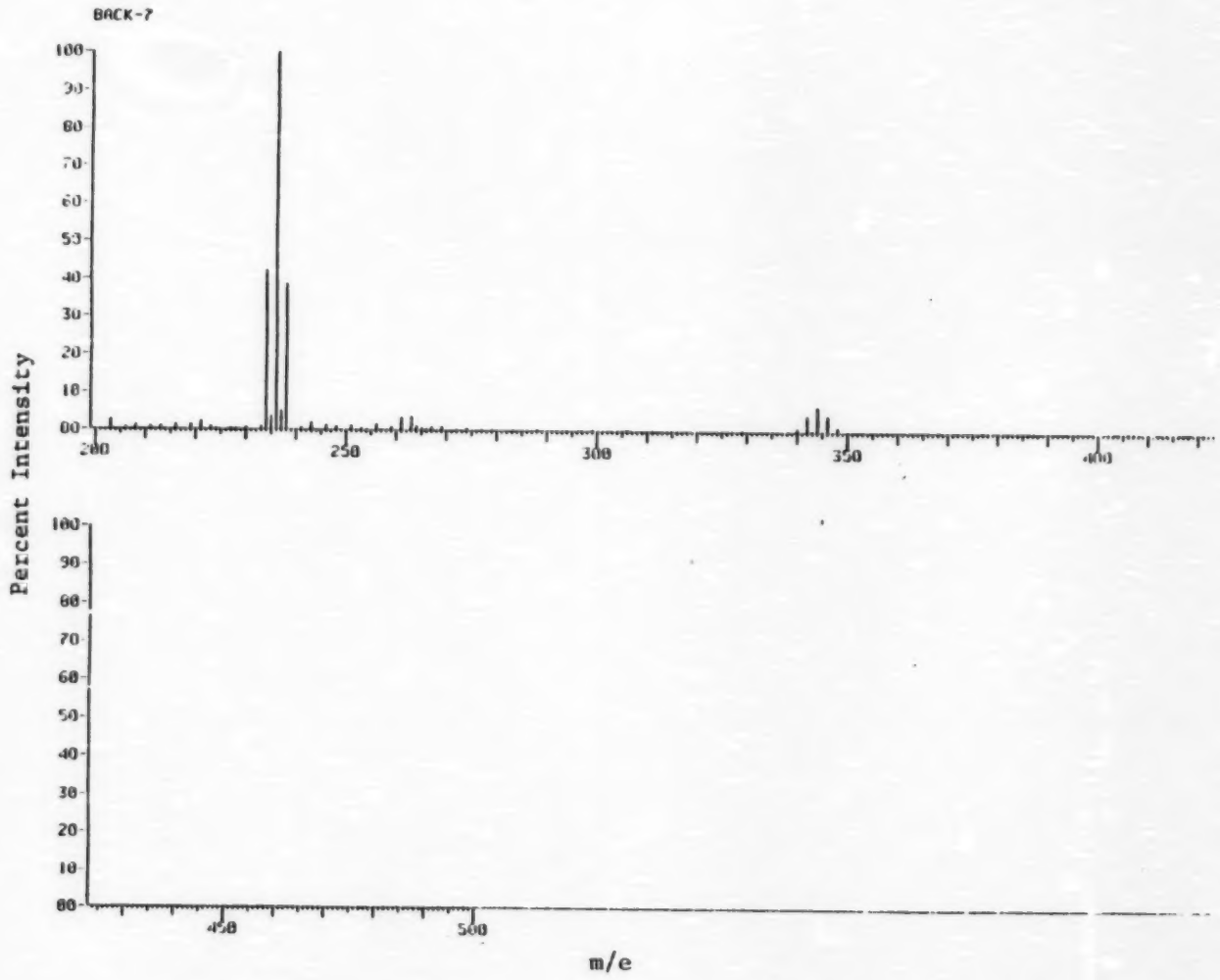

Figure B-2. Mass spectrum of dibromobenzene (MW=236) and tetrabromoethylene (MW=344).

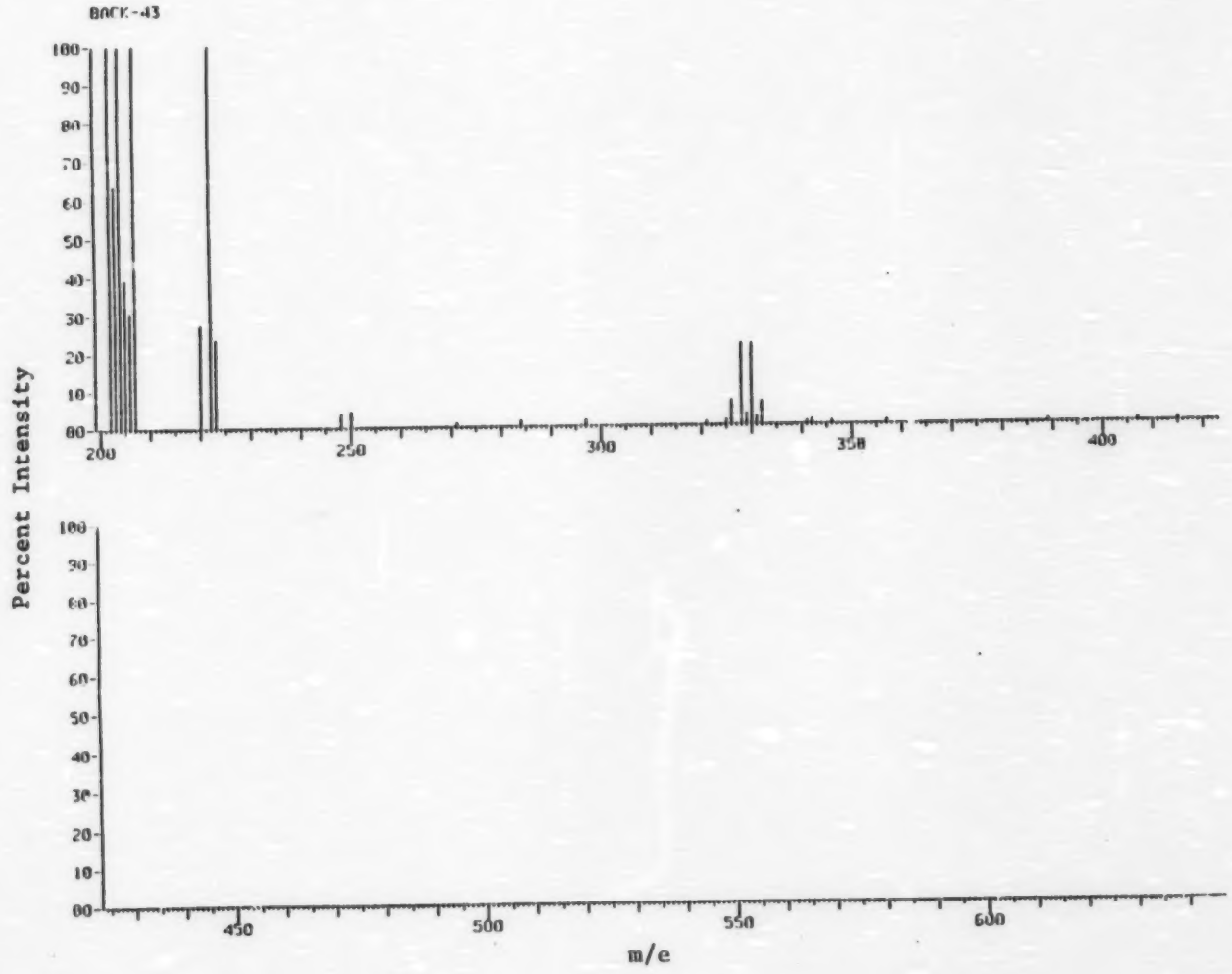

Figure B-3. Mass spectrum of $C_7H_5Br_3$ (MW=329).

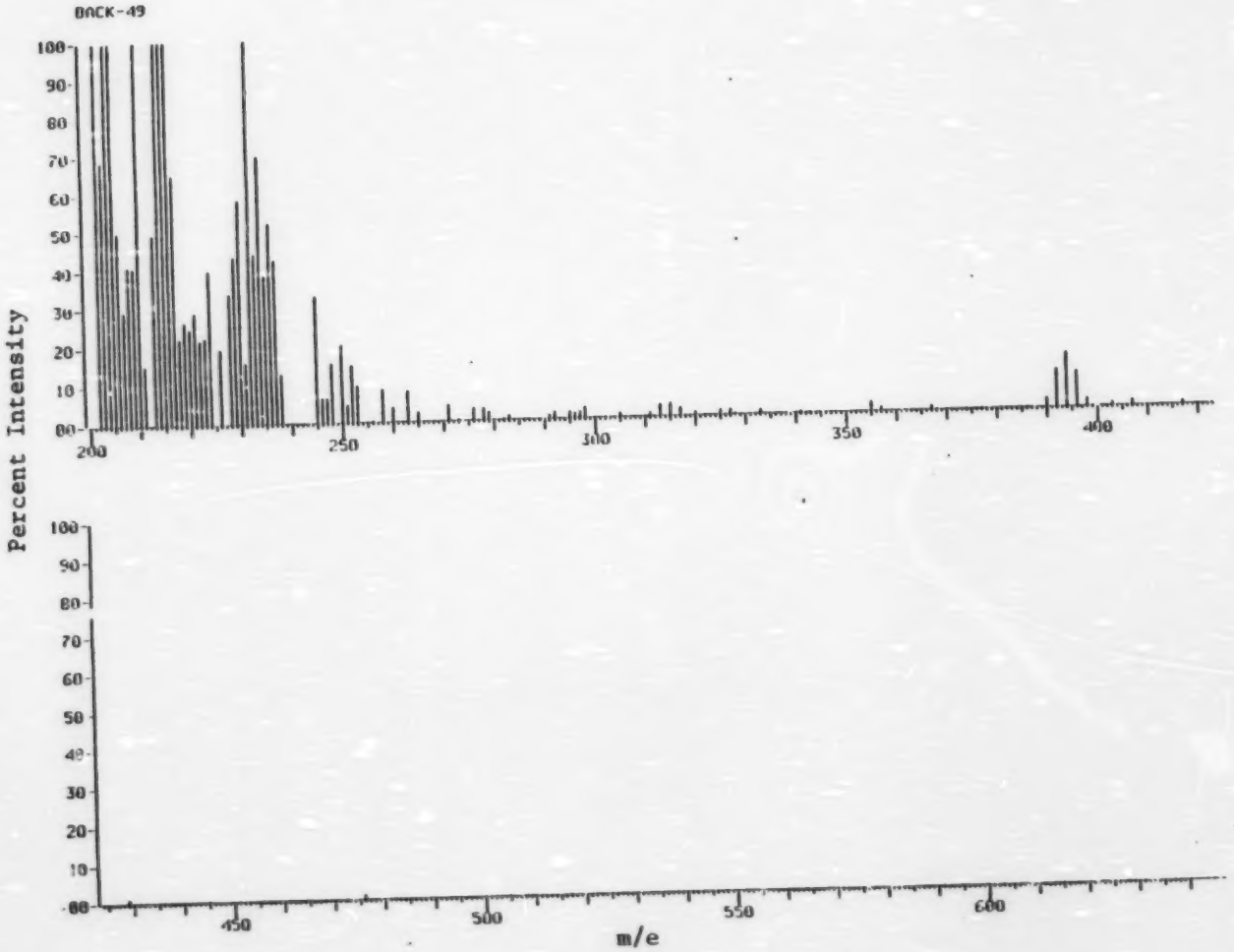

Figure B-4. Mass spectrum of tetrabromobenzene (MW=394).

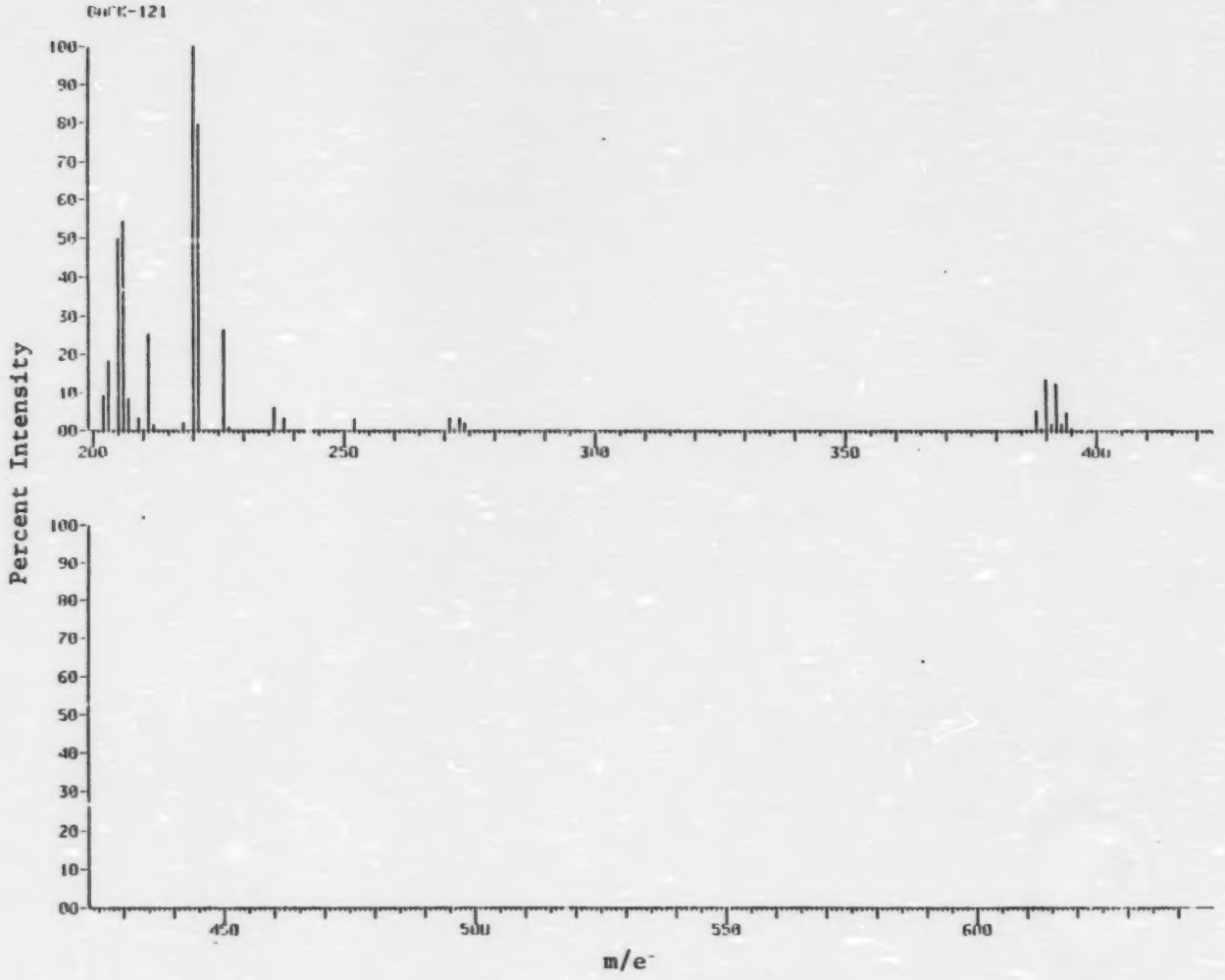

Figure B-5. Mass spectrum of tribromobiphenyl (MW=391).

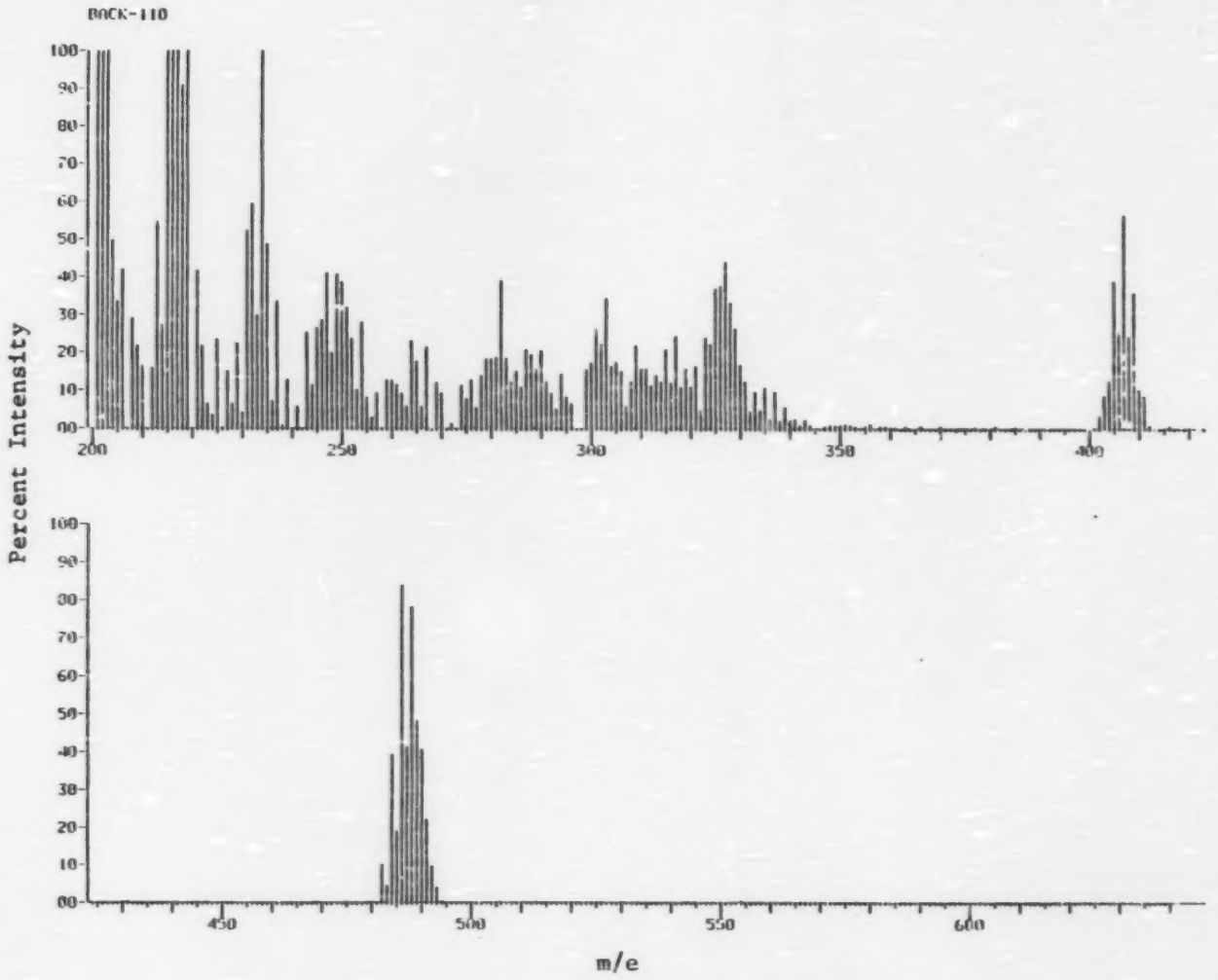

Figure B-6. Mass spectrum of $C_7H_3Br_5$ (MW=487).

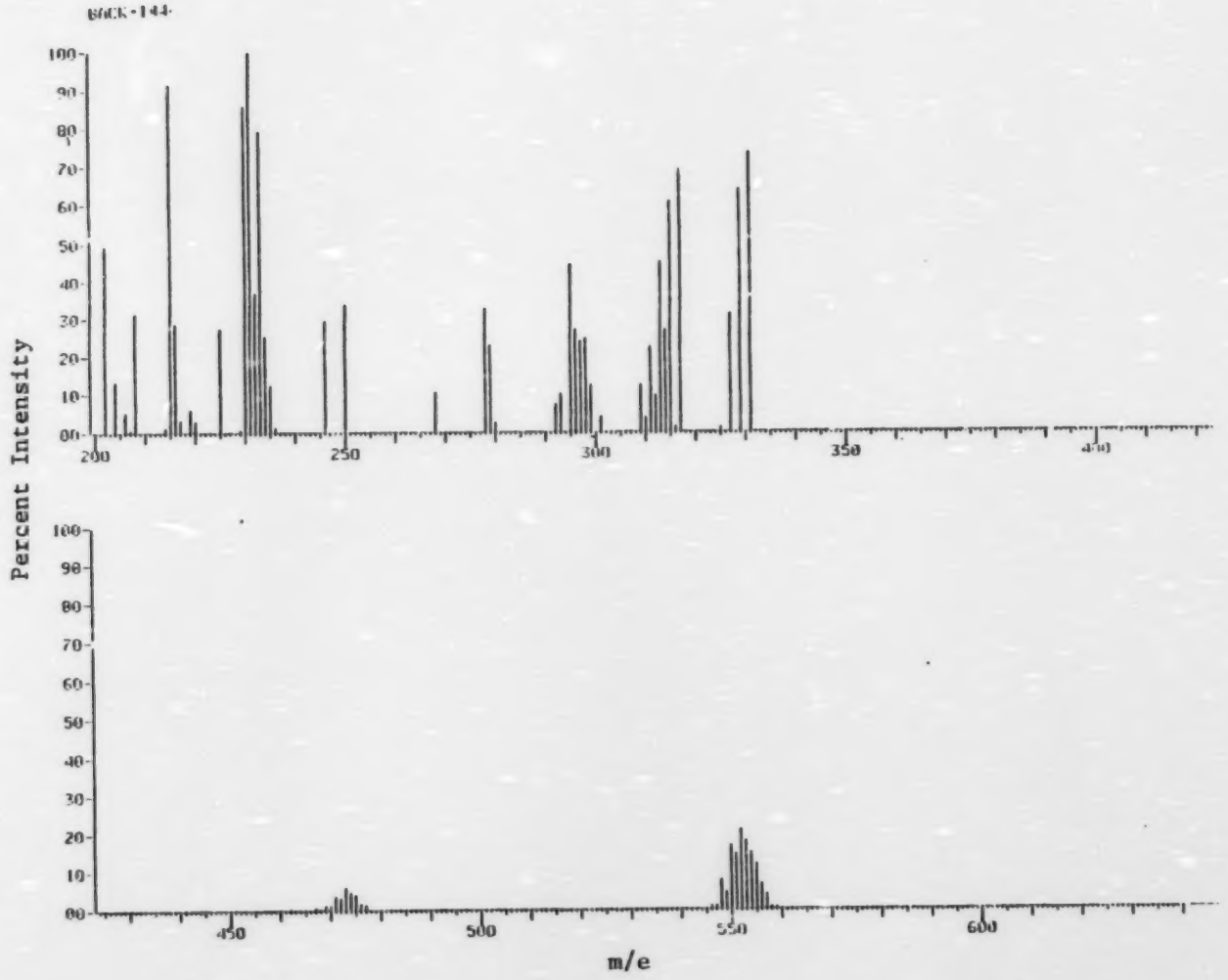

Figure B-7. Mass spectrum of hexabromobenzene (MW=552).

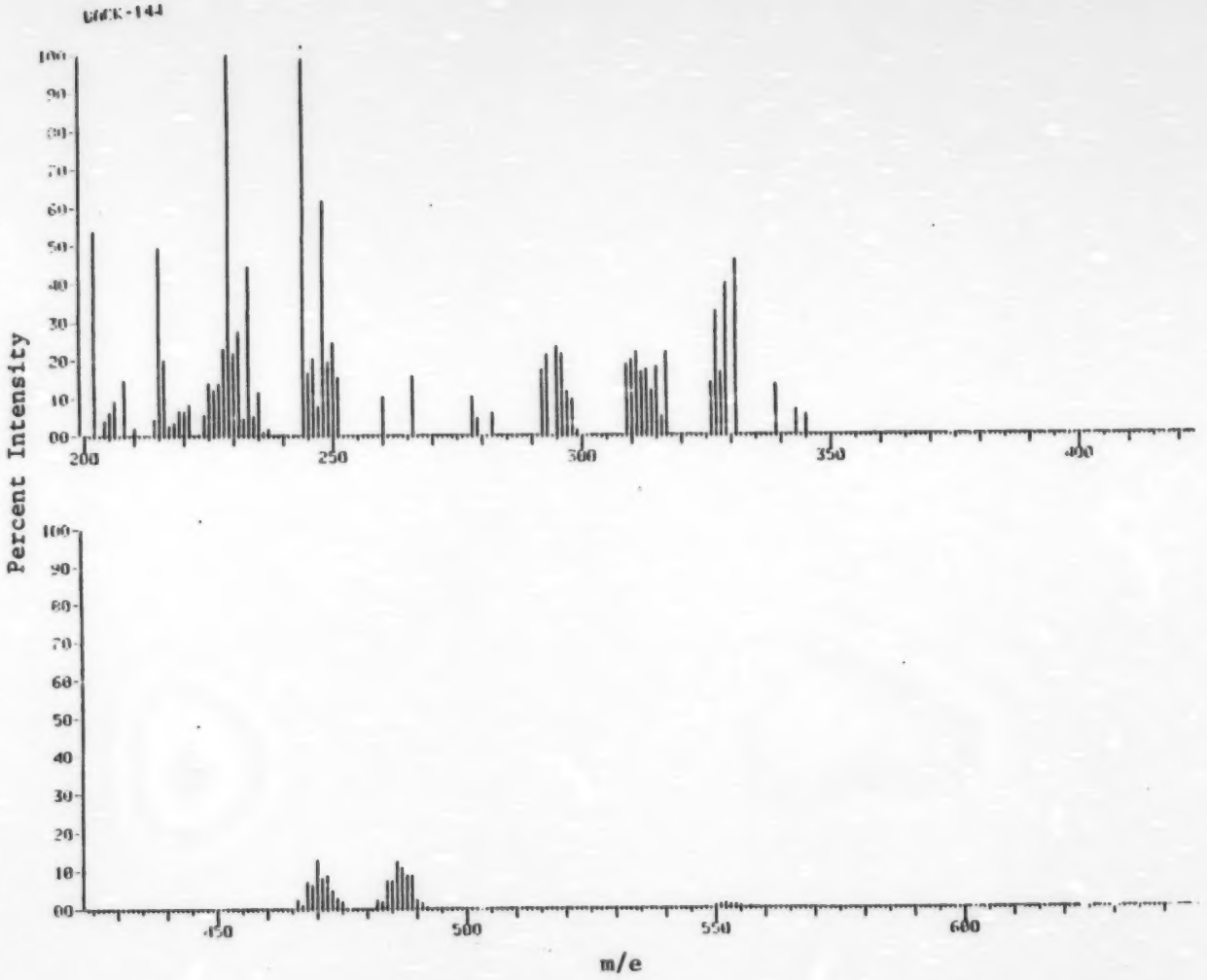

Figure B-8. Mass spectrum of tetrabromobiphenyl (MW=470) and $C_{12}H_6Br_4O$ (MW=486).

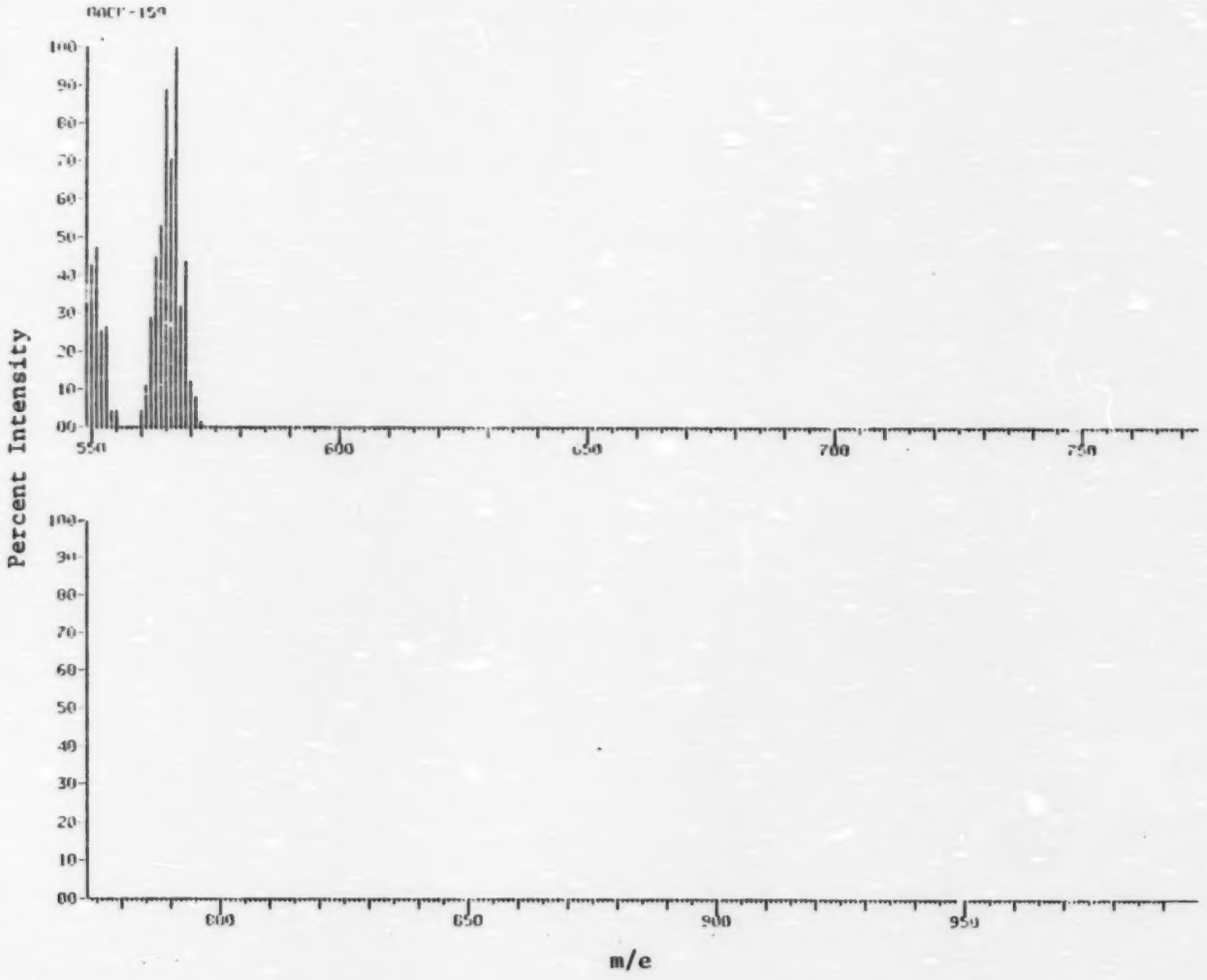

Figure B-9. Mass spectrum of pentabromobiphenyl (MW=549) and $C_{12}H_5Br_5O$ (MW=565).

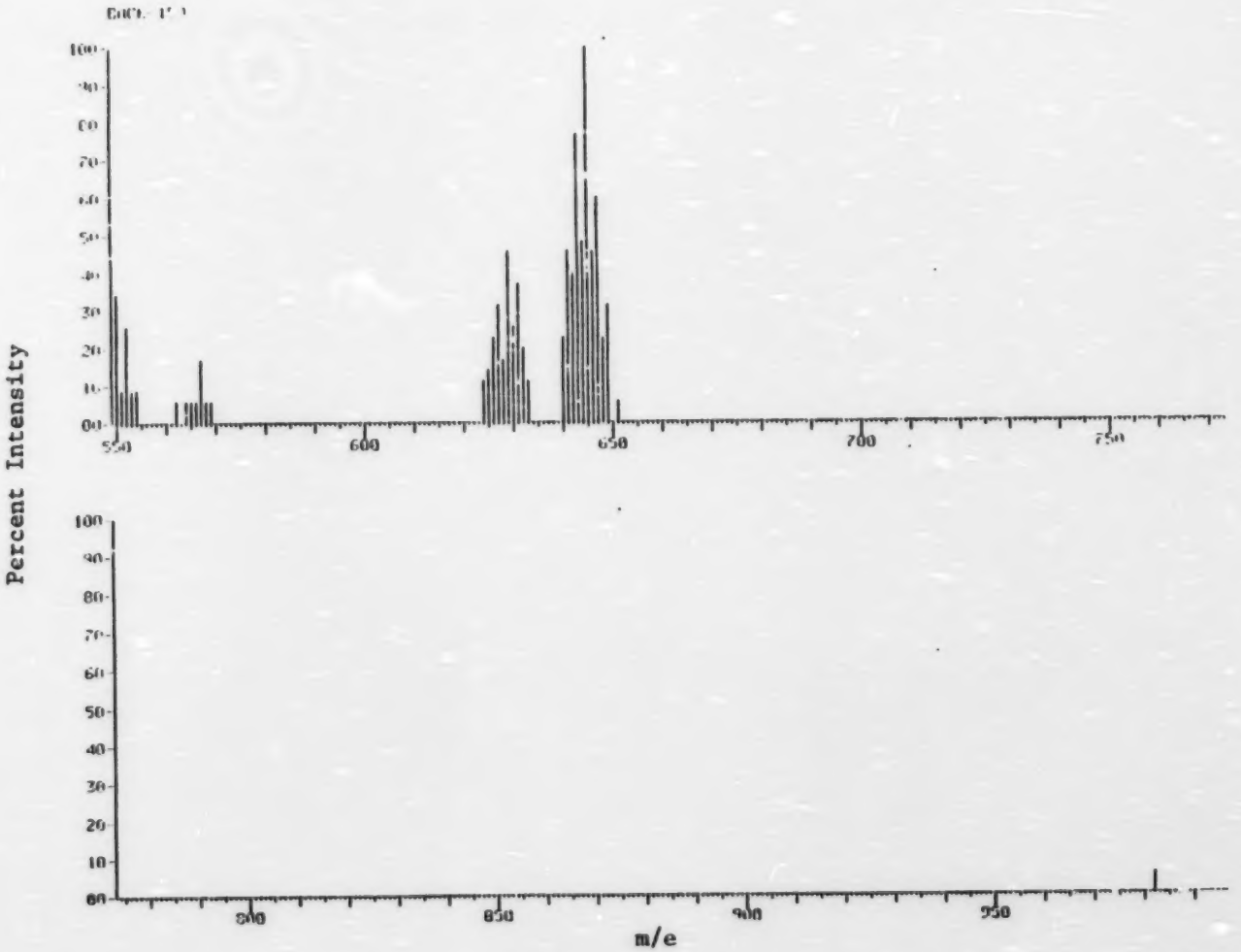

Figure B-10. Mass spectrum of hexabromobiphenyl (MW=628) and $C_{12}H_4Br_6O$ (MW=644).

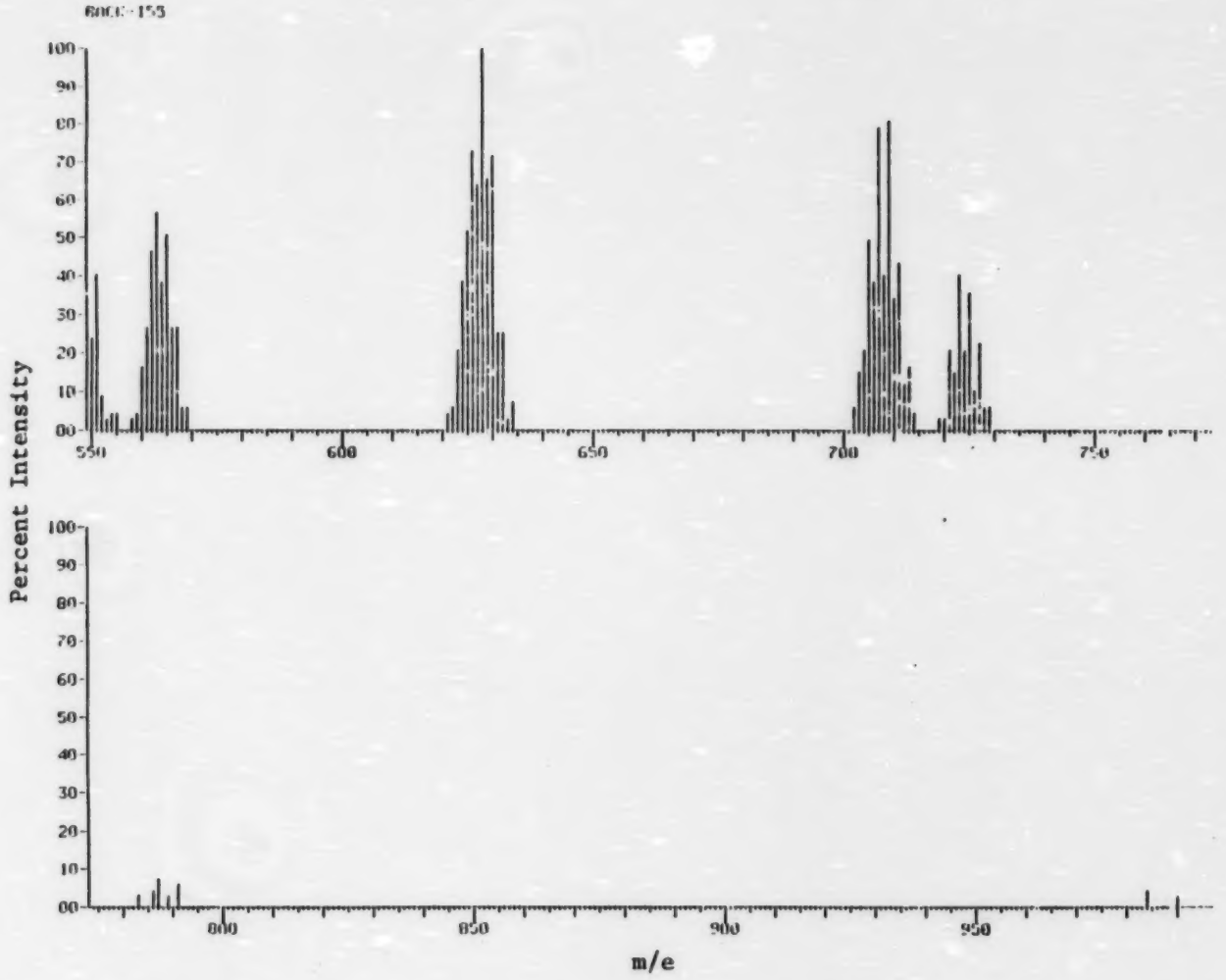

Figure B-11. Mass spectrum of heptabromobiphenyl (MW=707) and $C_{12}H_3Br_7O$ (MW=723).

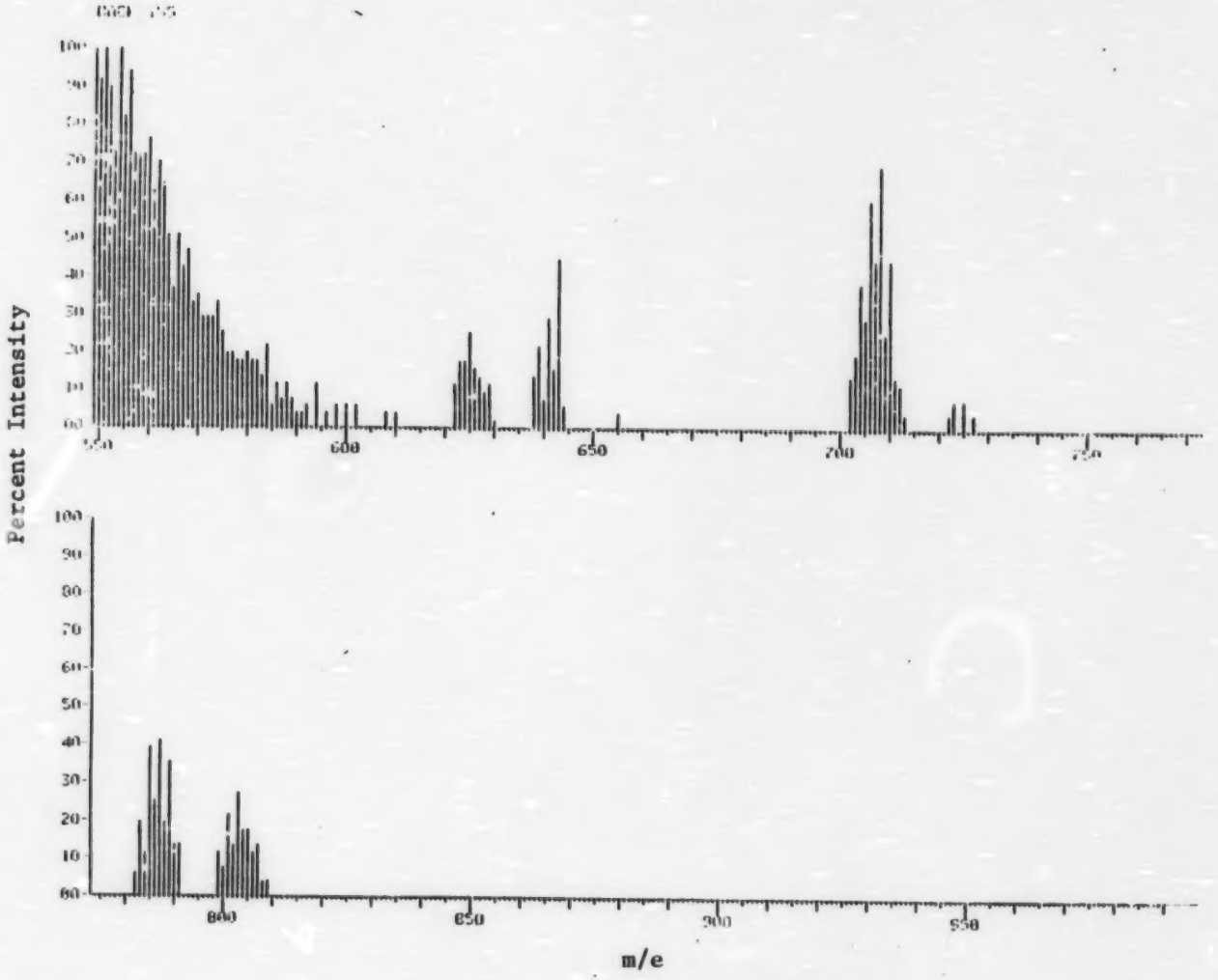

Figure B-12. Mass spectrum of octabromobiphenyl (MW=786) and $C_{12}H_2Br_8O$ (MW=802).

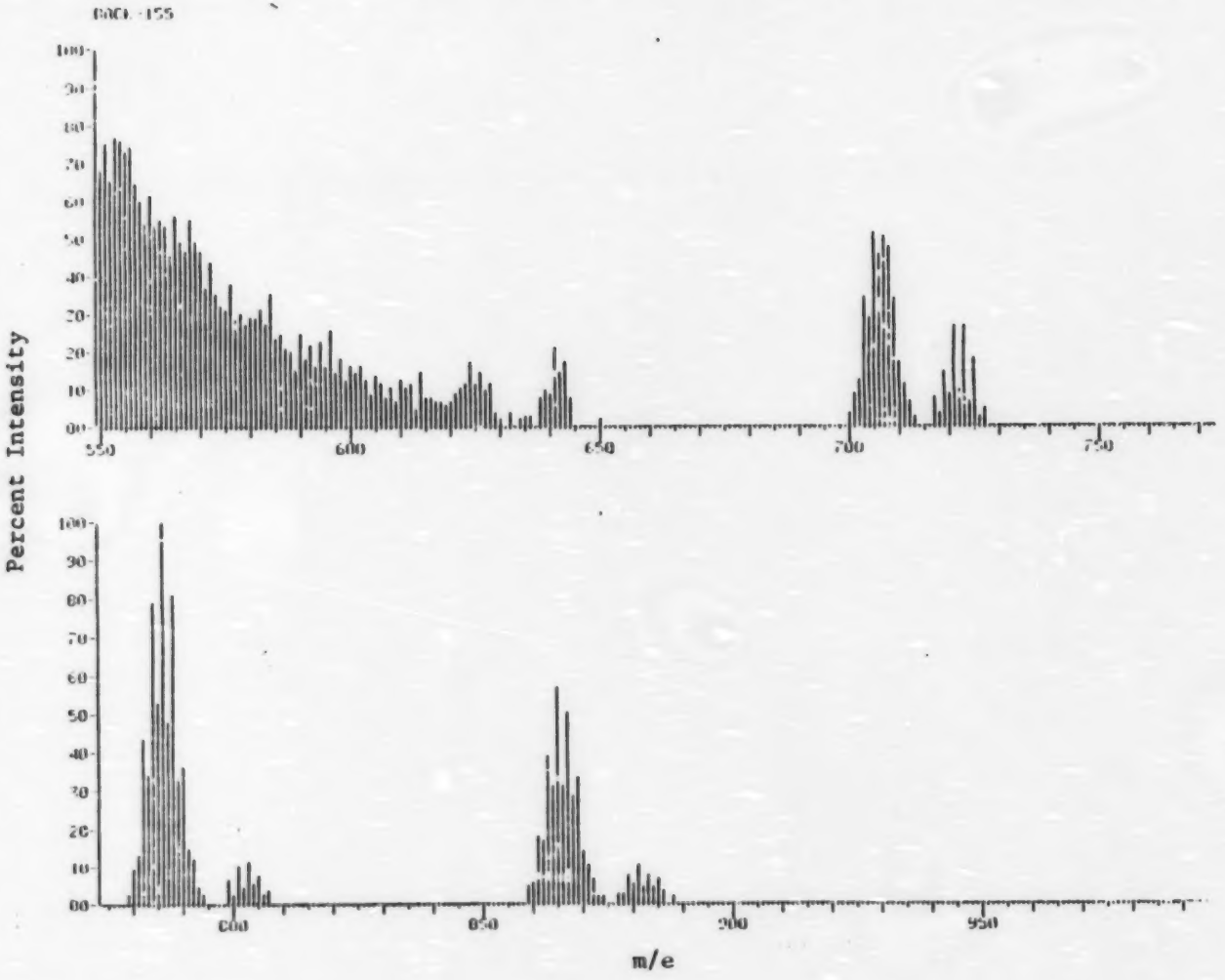

Figure B-13. Mass spectrum of nonabromobiphenyl (MW=866) and $C_{12}HBr_9O$ (MW=881).

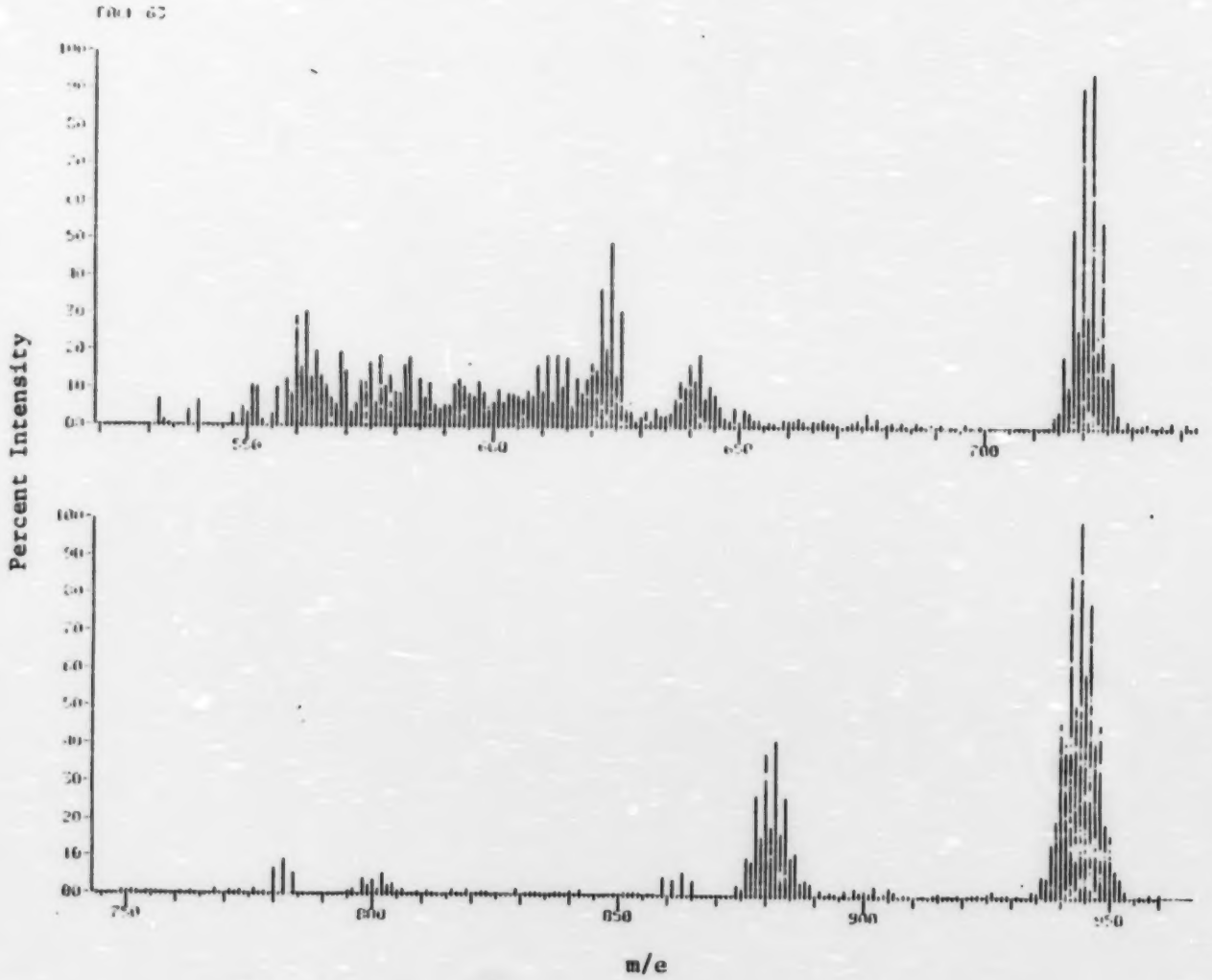

Figure B-14. Mass spectrum of decabromobiphenyl (MW=944).

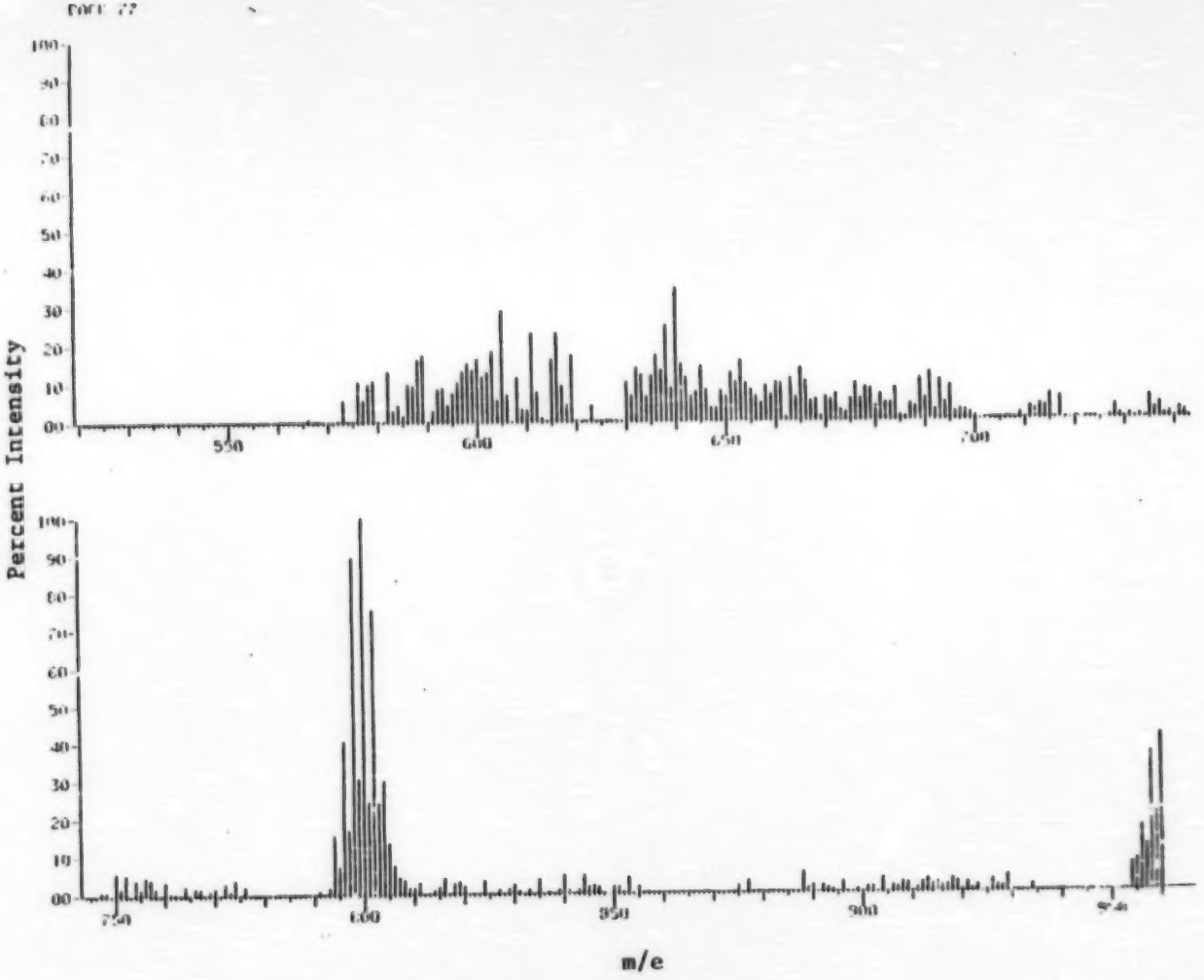

Figure B-15. Mass spectrum of $C_{12}Br_{10}O$ (MW=960).

APPENDIX C

REPRESENTATIVE MASS SPECTRA OF DECABROMOBIPHENYL ETHER AND IMPURITIES

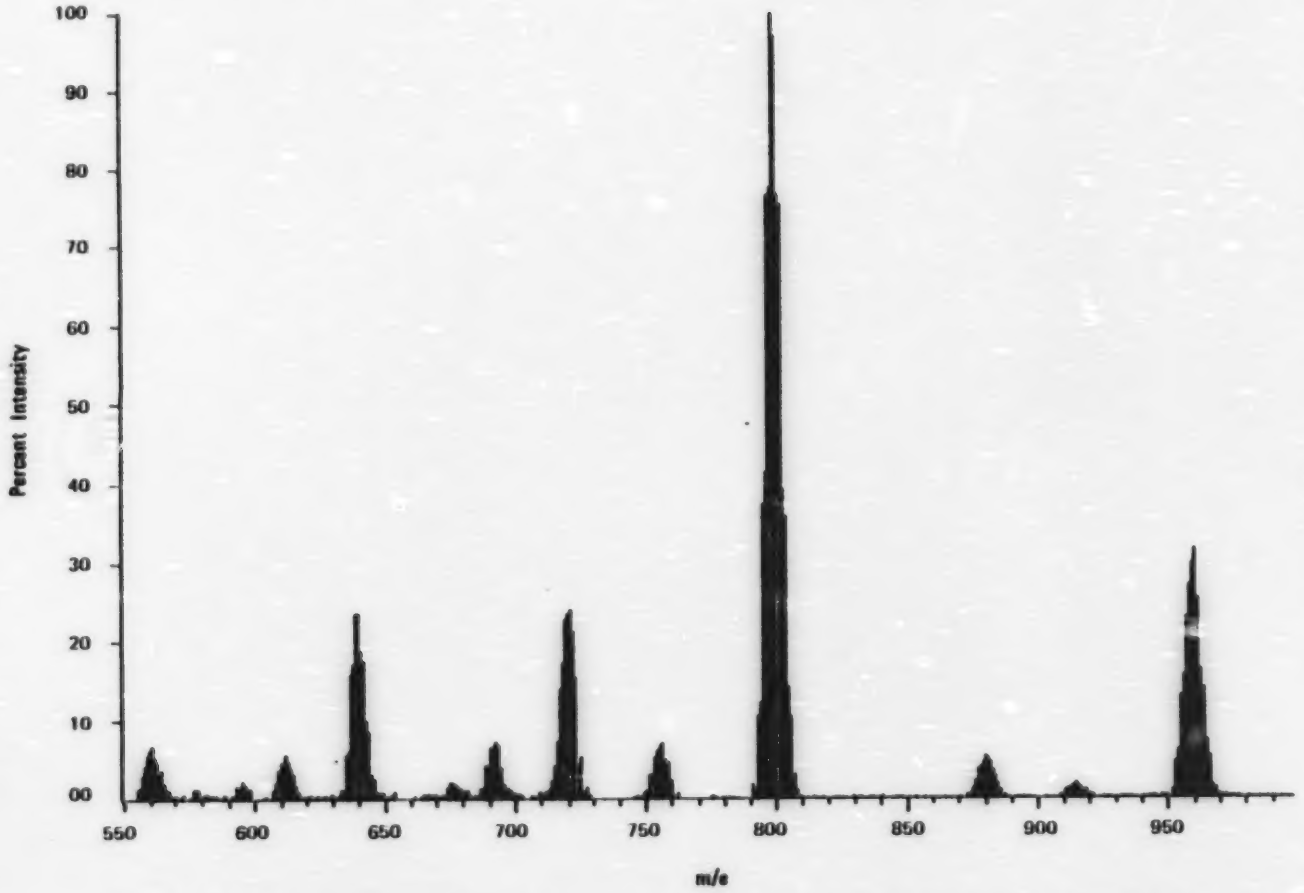

Figure C-1. Representative mass spectrum of decabromobipheny! ether $C_{12}Br_{10}$ (m/e = 960) and $C_{12}Br_9ClO$ (m/e = 914) which co-elute.

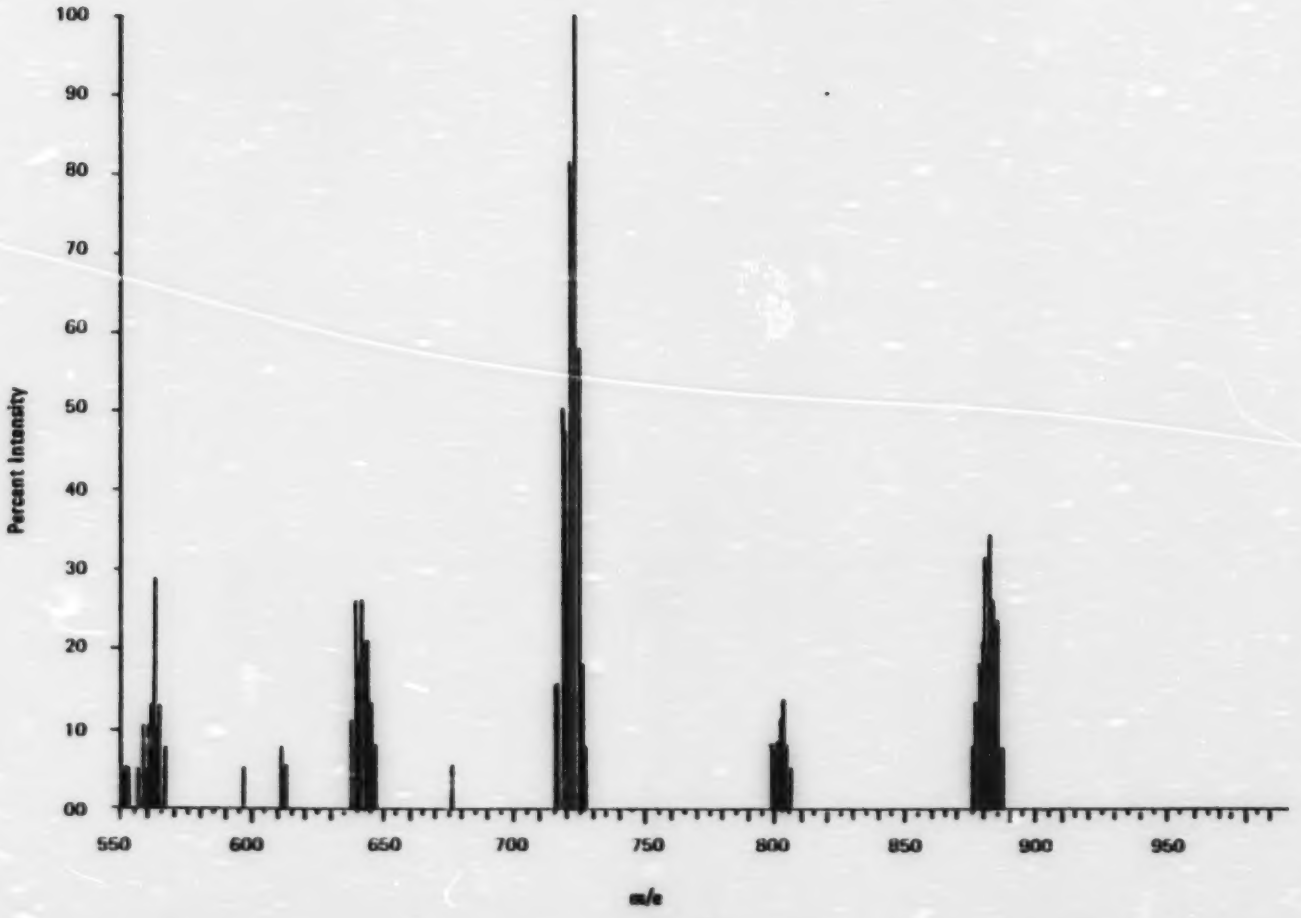

Figure C-2. Mass spectrum of $C_{12}Br_9HO$ (m/e = 880) found in DECABROM-DW sample.

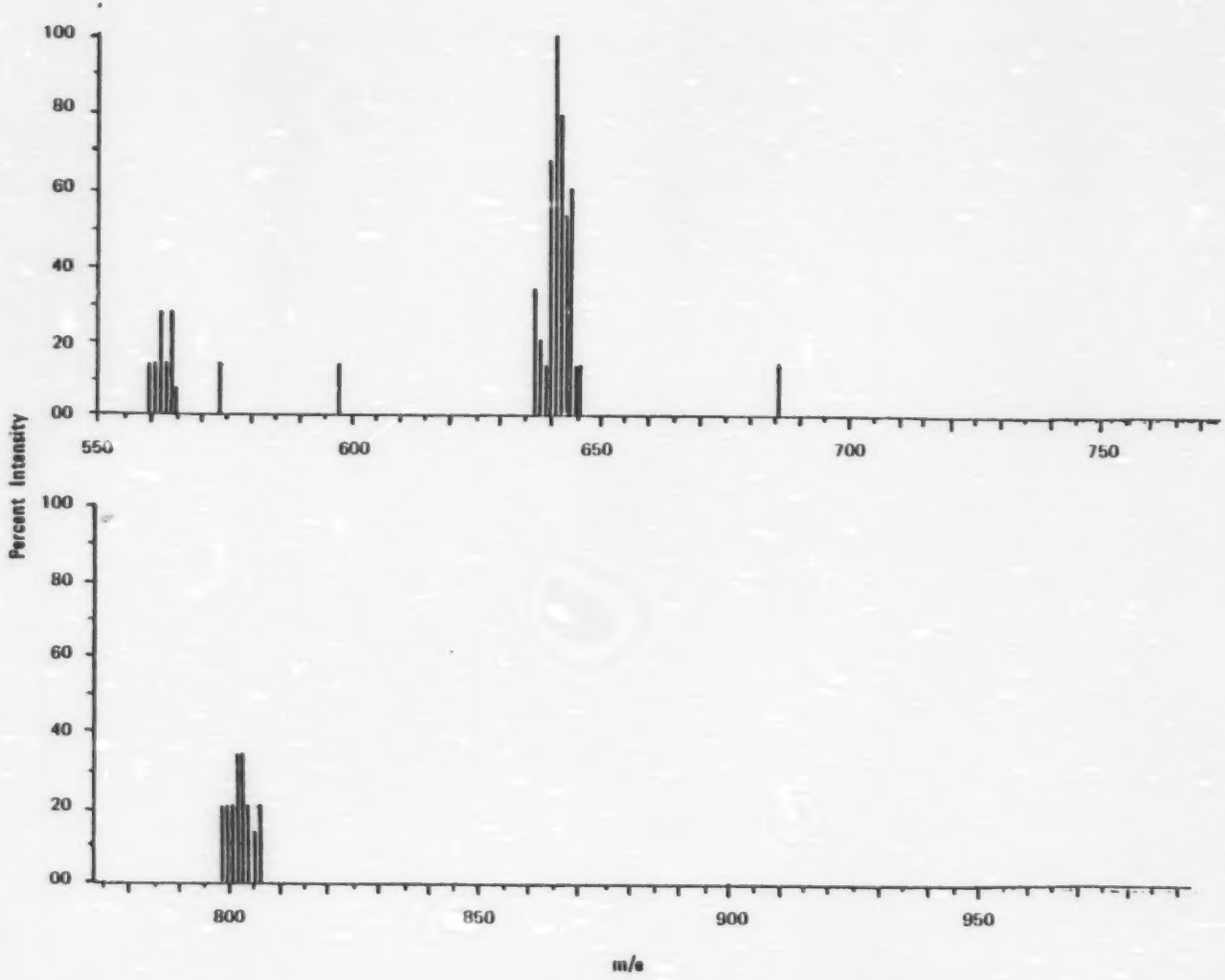

Figure C-3. Mass spectrum of $C_{12}Br_8H_2O$ (m/e = 802) found in DECABROM-DW sample.
Note: Trace amount of sample approaching the digitization level.